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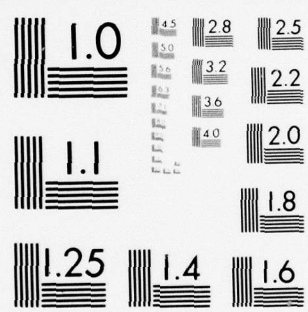

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DEPARTMENT OF THE NAVY OFFICE OF NAVAL RESEARCH TOKYO

DEPARTMENT OF THE NAVY O.N.R. TOKYO GROUP

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HIGH PRESSURE SCIENCE AND TECHNOLOGY IN JAPAN

EARL F. SKELTON
NAVAL RESEARCH LABORATORY

Department of the Navy
Office of Naval Research
Scientific Liaison Group - Tokyo

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This monograph represents an overview of the field of high pressure science and technology in Japan. It is based primarily on discussions held with scientists during on-site visitations to forty-three Japanese high pressure laboratories during the period from January to April, 1978. Particular attention is focused on the development of new or improved high pressure apparatus and efforts to synthesize super-hard materials via high

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pressure techniques, e.g., diamond and cubic boron nitride. Special note is also given to new or unusual high pressure data collection techniques; extended x-ray absorption fine structure and position sensitive proportional counters are two examples. Areas of scientific concern span the gambit from high pressure solid state physics and chemistry to studies of geophysical and biochemical reaction at elevated pressures. Appendices are provided with listings of Japanese scientists currently engaged in high pressure research and addresses of the appropriate institutional affiliations.

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As a consequence of (1) the pioneering character of this monograph which is the first Scientific Monograph to be officially published by ONR Tokyo, (2) the spirit of scientific cooperation and collaboration between ONR, NRL and ONR Tokyo which produced this document, and (3) the common desire to get the subject matter into print, all three of these organizations participated in the editing of this document. Major portions of the editorial work were done by the editorial group of the Naval Research Laboratory. (The manuscript was identified as NRL Paper 5280-27 for that work.) Additional editing was performed by members of the professional staff of the ONR Material Sciences Division. ONR Tokyo acknowledges both of these contributions with great appreciation.

Editorial Note

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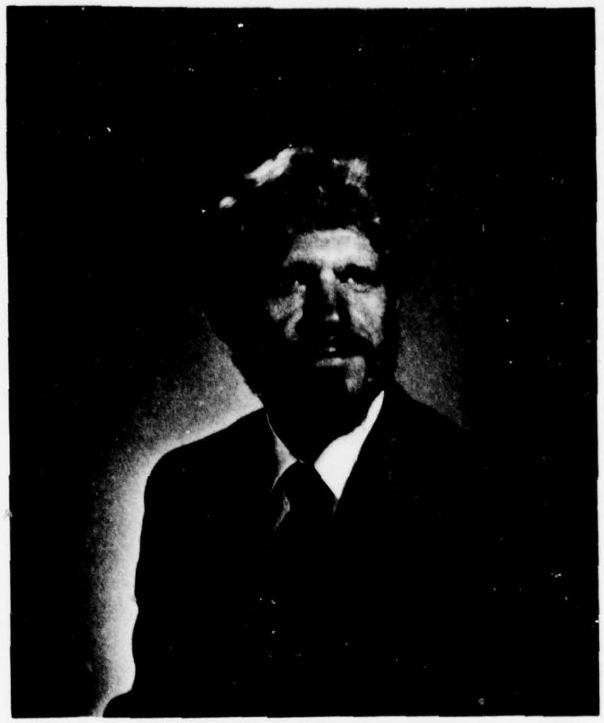

About the Author:

Dr. Earl F. Skelton was born in 1940, received his B.S. degree in physics from Fairleigh Dickinson University in 1962, and his Ph.D. degree, also in physics, from Rensselaer Polytechnic Institute in 1967. He came to the Naval Research Laboratory (NRL) as a Postdoctoral Associate of the National Academy of Sciences - National Research Council in the fall of 1967 to investigate lattice dynamical properties of selected rare earth materials. He is presently Head of the Phase Transformation Section in the Material Science and Technology Division at NRL.

Dr. Skelton's professional interests in high pressure research began as a graduate student, when he worked for several summers in the Army's high pressure laboratory at the Watervliet Arsenal. As a member of the Phase Transformation Section at NRL (formerally the High Pressure Section), Dr. Skelton has been interested in developmental studies of the diamond-anvil pressure cell with particular attention to applications involving cryogenic, x-ray, and electrical measurements. His research has resulted, thus far, in more than thirty publications covering such topics as pressure induced second-order phase transitions, high pressure energy dispersive x-ray diffractometry, high pressure-high temperature synthesis of superconducting materials, and pressure induced phase transitions in group III-V and II-VI semiconductors.

Some of his high pressure research is pursued in collaboration with the Laboratory for High Pressure Science at the University of Maryland, of which he is currently an Associate Member. He is also a member of the Washington Area High Pressure Colloquium and served as its chairman for three years. He was invited to serve on the organizing committee for the International Conference on High Pressure and Low Temperature held last summer and requested by the Director of Naval Materials to present a paper on future trends in high pressure synthesis at the recent conference of the International Association for the Advancement of High Pressure Science and Technology (AIRAPT).

In addition to his research activities, Dr. Skelton has been teaching for the past ten years at both the graduate and undergraduate levels on a part-time basis. He taught for five years in the Physics Department of Prince George's Community College and presently holds an Associate Professorial position at George Washington University in the Department of Civil, Mechanical, and Environmental Engineering and also teaches at the University of Maryland in the Department of Chemical Engineering.

On the amateur level, Dr. Skelton has a long standing interest in satellite communications via amateur radio. He is the recipient of seven awards for long range satellite communication and is currently serving as an officer and member of the Board of Directors of AMSAT, an international amateur satellite organization. This background provided an excellent basis for interaction with JAMSAT, a Japanese affiliate society of AMSAT.

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HIGH PRESSURE SCIENCE AND TECHNOLOGY IN JAPAN

Earl F. Skelton

Naval Research Laboratory
Washington, DC 20375

July, 1978

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Whatever degree of success may be realized from this treatise would not have been possible without the help of many people. At the Office of Naval Research, Dr. Edward I. Salkovitz, Director of the Material Sciences Division, and Dr. Arthur M. Diness, Director of the Metallurgy and Ceramics Program, are to be commended for their foresightedness in recognizing the importance of this scientific liaison and for their ability to develop the support necessary to authorize it. Drs. Salkovitz and Diness worked together to identify and commit the resources necessary to support the travel and, in addition, provided useful counsel and guidance. Equally important was the support provided by the Naval Research Laboratory during this sojourn; Dr. Alan Berman, Director of Research, and Dr. Albert I. Schindler, Associate Director of Research, and Director of Material and Radiation Science and Technology, are to be commended in this regard. I would also like to thank the staff of the Office of Naval Research - Tokyo, for easing the "cultural shock" and for providing a highly productive environment. I am indebted to Mr. Seikoh Sakiyama who provided expert Japanese diplomacy in handling many of the visitation details and also translated a number of technical articles from Japanese into English.

I would like to thank all of my Japanese hosts who widely opened the doors of their laboratories to me and were willing to discuss the details of their research in great depth. I owe a vote of special thanks to Professors Shigeru Minomura, Akifumi Onodera, and Taisuki Ito. Professor Minomura not only guided me through the research facilities of the Institute of Solid State Physics of The University of Tokyo, but he also permitted me to work in his laboratory for several days, thereby providing me with a "hands on" view of scientific research in Japan. I am indebted to Professor Onodera of Osaka University for kindly arranging all the details of my visits to the Osaka and Kobe areas, and to Professor Ito of Kyoto Institute of Technology for making similar arrangements in the Kyoto area. Special thanks are due to Professor Jiro Osugi of Kyoto University who also hosted my visit to the Kyoto area.

I am indebted to Drs. Joseph L. Feldman and Alan W. Webb of the Phase Transfromation Section, Naval Research Laboratory, for critically reading this monograph and the extensive assistance of Lahni N. Blohm in preparing the final manuscript is acknowledged in grateful appreciation.

ABSTRACT

This monograph represents an overview of the field of high pressure science and technology in Japan. It is based primarily on discussions held with scientists during on-site visitations to forty-three Japanese high pressure laboratories during the period from January to April, 1978. Particular attention is focused on the development of new or improved high pressure apparatus and efforts to synthesize super-hard materials, via high pressure techniques, e.g., diamond and cubic boron nitride. Special note is also given to new or unusual high pressure data collection techniques: extended x-ray absorption fine structure and position sensitive proportional counters are two examples. Areas of scientific concern span the gambit from high pressure solid state physics and chemistry to studies of geophysical and biochemical reactions at elevated pressures. Appendices are provided with listings of Japanese scientists currently engaged in high pressure research and addresses of the appropriate institutional affiliations.

I. INTRODUCTION

The purpose of this monograph is to review the field of high pressure science and technology in Japan. During the latter part of 1977, letters were sent to scientists involved in high pressure research at thirty-four Japanese research institutions. Based on the responses to these letters, and on personal contacts established while in Japan, visitations were made at forty-three laboratories, representing twenty-five institutions, during the period from January to April, 1978. A list of the laboratories visited and of the respective host scientists is given in Appendix D.

The objective of these visitations was to exchange information in the general area of high pressure science and technology. Formal seminars were presented at most institutions describing high pressure studies presently underway at the Naval Research Laboratory and the University of Maryland. The seminars covered recent research in the following areas: diamond-anvil pressure cell development, phase transitions in superconductors and metal-semiconductor systems, and superconducting materials synthesis. In other cases, the aforementioned topics were discussed informally.

In all instances, detailed discussions were pursued concerning the high pressure research underway in the hosting laboratory. The main text of this work, Part II, represents an attempt to summarize these discussions and to give a reasonably accurate picture of the research objectives, recent achievements, and current status of the various groups visited. It is to be noted that it was not the objective of this mission, nor is it the intent of this monograph, to critically review the high pressure research underway in Japan. Rather, this is an attempt to accurately relay and summarize the status of high pressure activities in Japan.

In the final section of this monograph, Part III, an effort is made to highlight some of the Japanese research programs which were found to be especially interesting and exciting. A strong attempt was made to carry out this evaluation objectively, but the reader must bear in mind, that this reviewer is a physicist with a strong materials science background. Apologies are offered to those researchers whose scientific research may have been very far afield from this reviewer's area of expertise and perhaps inadvertently excluded from special note.

It is assumed that the reader is somewhat familiar with current state-of-the-art high pressure equipment, as no attempt is made to explain such common high pressure facilities as Bridgman anvils, piston-cylinder, belt, girdle or multianvil devices. Three reviews on this subject are: High Pressure Methods in Solid State Research by C. C. Bradley (Plenum Press, New York, NY, 1969), Handbook of Techniques in High Pressure Research and Engineering by Daniil S. Tsiklis (translated from Russian by Alfred Bobrowsky; Plenum Press, New York, NY, 1968), and High Pressure Technology ed. by I. L. Spain and J. Paauwe (Marcel Dekker, Inc., New York, NY, 1978 - 2 vol.). One of the newest pieces of high pressure equipment, the diamond-anvil cell, is described in the review article by S. Block and G. J. Piermarini (Phys. Today, Sep., 1976; p. 44). It is also noted that, although many high pressure researchers still speak in terms of bars (1 bar = 10^6 dynes cm^{-2}), all pressures reported in this work have been converted to the SI unit of Pascal (1 Pa = 1 Nm^{-2}; 10 Kbar = 1 GPa).

II. INSTITUTIONAL REVIEWS

A. GIFU UNIVERSITY (GU)

1. Introduction

With a student enrollment of approximately 5000, Gifu University (GU) is typical in size to most Japanese national universities. Located in the city of Gifu, a little less than 30 km (about 18 miles) north of Nagoya, GU can be reached from Tokyo in about 3 hours: a two hour train ride followed by a one hour motor trip from Gifu-Hashima Station. The group visited is part of the Applied Electronics Section of the Department of Electrical Engineering; it is headed by Professor Sanji Fujimoto. The major high pressure research interests of this group are related to the electrical properties of materials.

2. Equipment

The high pressure equipment being used here consists of three main facilities: (1) a uniaxial press capable of pressures up to 1 GPa; (2) two hydraulic intensifier systems, each with variable temperature capabilities (one is operational up to 1 GPa and over the temperature range from 77 to about 290 K and the other is capable of pressures to 0.2 GPa and over the temperature range from 0 to 250 C); (3) a 300-ton belted piston-cylinder press with a maximum pressure capability of 3.5 GPa.

The pressures are determined in all cases by calibration of external load parameters against known (electrical) calibrants or from manganin coil pressure gauges. In the case of the low temperture studies, the procedure is to clamp the pressure at room temperature and then to cool the cell in a liquid-N_2 bath, followed by subsequent controlled electrical heating.

3. Research

Several types of high pressure measurements are performed at GU, e.g., dielectric constants, spontaneous polarizations, and uniaxial strains, the latter being determined from appropriate strain gauge measurements.

Pressure dependent dielectric properties have been measured as a function of applied frequency on the following systems: $CaCO_3$ (Fujimoto and Barnett, 1974a,b), KNO_2, $NaNO_2$, and $CaCO_3$ (Fujimoto et al., 1974), $Cu(HCOO)_2 \cdot 4H_2O$ (Fujimoto et al., 1975; Fujimoto et al., 1976; Fujimoto and Yasuda, 1976; Yasuda et al., 1978), NH_4LiSO_4 (Shimizu et al., 1977), $RbNO_3$ (Fujimoto et al., 1977), and $PbHPO_4$ and $PbHAsO_4$ (Yasuda et al., 1978). Generally speaking, each of these experimental studies is combined with a rather in depth theoretical evaluation of the data. Much of this work is summarized in recent phenomenological analyses of pressure induced ferroelectric and antiferroelectric transitions in terms of free energy considerations. (Fujimoto and Yasuda, 1974, and Fujimoto and Yasuda, 1976b). In the case of ferroelectric transitions, the free energy is expressed by modifying Devonshire's free energy expansion for hydrostatic pressures. The resulting expressions can be used to predict both the pressure and the temperature dependence of the electrical permittivity and the spontaneous polarization.

In the case of the antiferroelectric transitions, the free energy is expanded in terms of the pressure, the polarization, and the electric field strength and, after determination of up to six phenomenological parameters, the pressure dependence of the permittivity or spontaneous polarization may be evaluated. This treatment also provides phenomenological explanation of some of the observed pressure induced hysteresis phenomena for first- and second-order antiferroelectric transitions.

4. Summary

The work at GU is dedicated to detailed studies of dielectric materials and although the high pressure equipment has not been "new" for many years, this laboratory continues to generate quality, publishable work. Like many laboratories visited, it is conscientious analyses and interpretations of reasonably accurate, albeit sub-5 GPa, high pressure data which result in the continued output of high quality results. There do not appear to be any plans for major changes in the direction or composition of this group in the immediate future.

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B. HIROSHIMA UNIVERSITY (HU)

1. Introduction

Hiroshima University (HU) was created in 1949 from a number of schools in the Hiroshima Prefecture, the oldest school of which, Hiroshima Prefecture Normal School, was founded in 1875. HU is the only government supported school in this prefecture and it ranks eighth in size among government supported universities. It consists of nine faculties and five research institutes, representing approximately 11,000 students. At present HU has several campuses in various parts of the prefecture, but construction will soon begin at centrally located Saijo where the various campuses will ultimately be consolidated.

High pressure work at HU is found in the Department of Material Sciences on the main campus in Hiroshima city. Professor Hiroshi Fujiwara directs several groups, two of which are engaged in high pressure research. High pressure Group I is headed by Dr. Motoyuki Nomura and is concerned with phase diagrams and high pressure techniques in general. Currently this group is particularly concerned with problems of shear stresses in the pressure environment. Dr. Hideoki Kadomatsu is the leader of High Pressure Group II; the effects of pressure on various magnetic properties are the primary interests of this group.

2. High Pressure Group I

The general interests of this group are related to solid-solid phase transformations, but as an outgrowth of this, considerable attention has been focused recently on the problems involving non-hydrostatic pressures. The main tool being used to investigate this problem is a cubic-anvil press similar to the one developed by Inoue and Asada (cf. part II-G). A 500-ton press, manufactured by Kobe Steel, Ltd., is used in conjunction with both 10, 8, and 6 mm cubic anvils; the ultimate pressures range from 5 to 8 GPa with decreasing anvil size. The cubic anvils compress a cell made of amorphous boron solidified with epoxy in which the polycrystalline specimen is contained.

X-rays from a fine focus Mo or Ag target are collimated by a 0.3 mm slit and enter the pressure cavity through one of the vertical cube edges; the scattered radiation is analyzed through a $\pm 40^{\circ}$-window in 2θ with a scintillation counter in a step-scanning mode.

Preliminary studies have been carried out on the compressibility of several Ni- and Fe-based alloys (Nomura et al., 1976). Using NaCl as an internal pressure standard, it was found that an anomalous bulge in the pressure dependence of the lattice parameter was produced in all Ni and Fe alloys which were given an initial, residual strain. Investigation of this problem continues.

Continuing an examination of the effects of a non-hydrostatic pressure medium, Yamamoto et al., (1977) measured the linear compressibility of Si to 6.5 GPa. In this experiment, the sample was encapsulated in several

different fluid transmitting media which, in turn, were contained within the boron-cube. It was found that the apparent compressibility of Si actually increased at elevated pressures where the pressure transmitting fluid entered a glassy state. Yamamoto et al. have suggested that, based on x-ray line broadening, the Si may be deforming to an orthorhombic structure at elevated pressures because of the presence of internal shear stresses, although other interpretations may also be possible.

In a very recent study, Nomura et al. (1977) have examined the widths of hysteresis loops in various potassium halides. For example, in KCl they find that, in a hydrostatic pressure medium of iso-propanol, the transition pressure ranges from 2.53 to 1.66 GPa depending on whether the pressure is increasing or decreasing, respectively. The hysteresis loop itself is shown in Fig. II-B-1. Although a detailed explanation of the P-V hysteresis loops in these potassium halides remains an open question, it might be interesting to attempt to measure the temperature dependence of the loop width and possibly obtain information about the activation energy for this transformation. Work on this problem, in addition to a general investigation of the effects of non-hydrostatic pressure environment, continues in this group.

3. High-Pressure Group II

The main focus of the second high pressure group at HU is directed toward magnetic properties of solids. In particular, various magnetic transitions, e.g., the ferro-antiferromagnetic (T_f), the ferro-paramagnetic or Curie (T_c), the antiferro-paramagnetic or Néel (T_n), and the paramagnetic Curie (Θ) temperatures, can be measured as a function of pressure up to 600 or 700 MPa and to temperatures as low as 4.2 K. Detection of these transitions is by induction measurements using a Hartshorn bridge circuit. The pressure is generated in an external, hydraulic press, transmitted to a Be-Cu pressure bomb by petroleum ether, and measured with a manganin resistance gauge. The complete details of the system are given in the paper by Fujiwara et al. (1970).

The most recent work of this group has been on the pressure dependence of T_c for a series of Ni-based alloys, viz., Ni-V, -Cu, -Pd, -Pt, and -Rh. In all cases (dT_c/dP) was found to decrease monotonically with increasing solute concentration. Based on the T_c dependence of (dT_c/dP), Fujiwara et al. (1976) are able to deduce detailed information concerning the effect of pressure on the electionic energy bands in these systems.

In an even more recent study, Fujiwara et al. (1977) have examined the pressure dependence of the magnetic properties of a number of heavy rare earth binary alloys. From careful measurements of the pressure derivatives of T_f, T_c, T_n, and Θ, this group has evaluated the pressure coefficient of the effective number of Bohr magnetons and correlated this information with the average number of 4f-electrons in the various systems studied. These results are then discussed in terms of molecular field theory.

Similar studies are currently underway on selected 3d-transition metal semi-borides, e.g., $(Co_{1-x}\ Mn_x)_2\ B$. Future plans call for the development

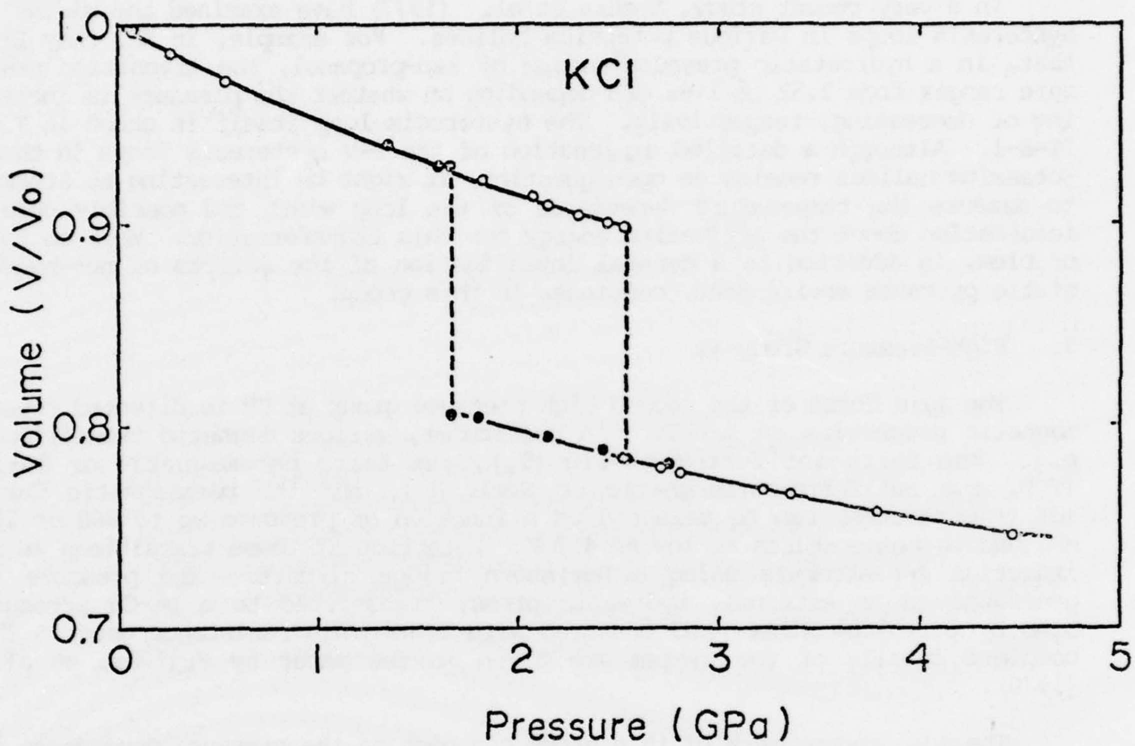

Fig. II-B-1: Pressure - volume hysteresis loop of KCl observed under hydrostatic pressures. Open and closed circles refer to increasing and decreasing pressure runs, respectively (from Nomura et al. 1977).

of techniques for (1) measuring the pressure dependence of spontaneous magnetization, (2) analyzing pressure dependent magnetic-transition temperature data in a unified and systematic manner, and (3) measuring pressure effects on magnetocrystalline anisotropy at reduced temperatures.

4. Summary

These two high pressure groups have a very positive and aggressive attitude toward their research; much of this may be attributed to their leader, Professor Fujiwara. They give the impression of being honestly concerned with understanding the complete details of every facet of their data. It is just this attitude that has led to the very interesting studies on the effects of a non-hydrostatic pressure medium and the curious observation of the large P-V hysteresis in the potassium halides.

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C. Hitachi, Ltd. (HL)

1. Introduction

The response to the initial inquiry regarding high pressure research at Hitachi, Ltd., (HL) was negative. However, through the efforts of Dr. A. M. Diness*, it was learned that there is work underway in the Central Research Laboratory of HL on high pressure synthesis of BN. The following summary is based, in part, on information supplied by Dr. Kenzo Susa of HL.

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*On temporary assignment to ONR-Tokyo.

2. Boron Nitride

High pressure synthesis studies on BN have been underway at HL for several years. Particular attention has been focused on the effects of catalysts on the synthesis conditions. The overall objectives of the work appear to be directed toward improving the reaction conditions necessary for the synthesis of cubic-BN, i.e., to find the minimum pressure and temperature required for transformation of graphite-type BN structure to the cubic form (g-to-c).

Using both girdle-type and cubic anvil presses equipped with internal graphite heaters and pyrophyllite gaskets, Drs. Kenzo Susa, Toshio Kobayashi, and Satoshi Taniguchi have performed a large number of BN-synthesis experiments and analyzed the quenched products by means of both x-ray diffraction and electron microscopy techniques. Initially, Susa et al. (1974a,b) showed that water can be used as an effective catalyst in the g-to-c conversion. In particular, a water content of about 40 wt-% reduced the minimum reaction temperature to about 600 C (at 5 GPa), which is significantly less than the 800 C required (at 3 GPa) for Ag-Cd and Sn-Cu catalysts. Based on x-ray line broadening data, the resultant c-BN crystallites were estimated to be very small in size.

Subsequent examinations of the reaction products led Susa et al. (1975 & 1976) to suggest the formation of anhydrous ammonium borate as an intermediate phase, serving as a flux for the g-to-c conversion. This, in turn, led to the discovery of other, more effective, catalysts, viz., urea ($(NH_2)_2CO$), ammonium nitrate (NH_4NO_3), and ammonium borate ($(NH_4)_2B_4O_7$). Moreover, it was found that c-BN could be produced, under similar (P,T)-conditions, with only boron and urea or ammonium nitrate as starting materials.

Additional experiments to further describe the reaction mechanism were performed by Kobayashi et al. (1977) with c-BN as a starting material. This work indicated that there is a wide temperature range for the g-c phase boundary at 4.2 GPa, this pressure also corresponds to the minimum necessary for the c-BN synthesis using water as a catalyst.

Most recently, the crystallites produced with both water and urea catalysts were examined by Susa et al. (1978) and Kobayashi et al. (1978), respectively. Crystallites produced with water at 800 C and 6 GPa were about 100 A in diameter and increased in size with increasing reaction temperature to about 0.4 μm at 1500 C. In the case of urea, the crystallite sizes ranged from 0.02 to 0.7 μm with reaction temperature increasing from 900 to 1800 C at 4.3 GPa.

Work on c-BN synthesis continues at HL with increasing attention being focused on the catalytic systems and the chemistry of the reaction. It would undoubtedly be very helpful to have <u>in situ</u> data so as to more precisely characterize the g-to-c conversion mechanism. Such capabilities are now being used in the BN and diamond synthesis programs underway at Kobe Steel, Ltd. (cf. Part II-G).

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D. HOKKAIDO UNIVERSITY (HKU)

1. Introduction

Hokkaido University (HKU) was founded in 1876 as the Sapporo Agricultural College, but its origin can actually be traced four years earlier to the Hokkaido Development Office Temporary School which was created in 1872 for the purpose of training pioneers to open up and develop the island of Hokkaido. The main campus at Sapporo bears a very strong resemblance to a typical New England university; this is due in large to the strong influence of its first vice-president, Dr. William Smith Clark. As part of the Japanese national university system, HKU today has a total student enrollment in excess of 12,000.

There are three groups at HKU engaged in high pressure work, all located on the main campus at Sapporo; these are found in the Department of Geology and Mineralogy, the Department of Physics, and the Research Center for Earthquake Prediction.

2. Department of Geology and Mineralogy

Until recently the bulk of the high pressure research in this department has been carried out under the guidance of Professor Kenzo Yagi. However, on April 1, 1978, Professor Yagi retired from a 40 year career in the field of mineralogical science. He is aptly succeeded in this department by Professor Yu Hariya who is continuing many of the high pressure programs.

There is an abundance of high pressure research equipment being used by this group: four opposed anvil presses, the largest having a maximum load of 500-tons, a piston-cylinder device made by the Shimadzu Co. which can be operated to 5 GPa and 2000 C, ten hydrothermal reaction chambers capable of

pressure and temperature limits of 300 MPa and about 1000 C, respectively, and an assortment of various x-ray gear. It is interesting to note that for many of the high temperature runs in the piston cylinder apparatus, molten Pyrex glass is used as the pressure transmitting medium.

The main research interests in this group center around experimental mineralogy and petrology. In one recent investigation, Arima and Onuma (1977) measured the solubility of alumina in enstatite in the pressure, temperature range 1-2.5 GPa and 1100-1500 C, respectively. It was learned from this work that the alumina content in enstatite coexisting with sapphirine and quartz increases with increasing pressure and temperature, while that in enstatite co-existing with sapphirine and sillimanite, decreases with increasing pressure and decreasing temperature. An important conclusion reached in this study is that, in order to use the alumina content of orthopyroxene as either a pressure or temperature indicator, appropriate consideration must be given to the specifics of the mineral assemblage.

In another very interesting study, the details of which have not yet been published, the ratios of deuterium-to-hydrogen in selected silicate melts are examined as a function of pressure. This work is important in determining the role of water in the mantle or lower crust of the earth. The D/H-ratios are referenced to the relative standard mean ocean water in per mil units. In measuring the pressure dependence of the water content in certain silicate minerals, it was found that in quartz the D/H-ratios ranged from -40 to -20, whereas in albite the range was from +20 to +40. (The starting water had a value of -75.1 to -78.0 per mil; see Fig. II-D-1.) There is no explanation offered for this large variation in the D/H-ratios of these silicate glasses and the only conclusion that Hariya et al. (1978) are prepared to draw at present is "... that the fractionation of hydrogen isotope between crystal, liquid, and vapor in (the) upper mantle or lower crust is rather complex."

Other high pressure studies recently concluded in this department include an examination of the kyanite-sillimanite transition with excess quartz and correndum (Hariya and Arima, 1975), the stability relation in kaersutite (Yagi et al., 1975), decomposition of $CaFe^{3+}AlSiO_3$ pyroxene at elevated pressures and low oxygen partial pressure (Ohashi and Hariya, 1975), and the effect of pressure on the water content of amphiboles (Kuroda et al., 1975).

3. Department of Physics

The high pressure research in the Department of Physics at HKU had been led by Professor Tadayasu Mitsui but unfortunately he died of cancer in June, 1976. Work in this unit is now directed by his successor, Professor N. Mori.

There is some unique high pressure equipment being used in this department; for example, the only high pressure system capable of simultaneous low temperature x-ray measurements seen in Japan by this reviewer is here at HKU. Endo and Mitsui (1974) have designed a clamp-type cell made of Be-Cu, which uses a pair of WC Bridgman anvils and is capable of producing up to 15 GPa pressure. Two 100^{o} slots are provided for appropriate x-ray scattering measurements and the anvils are electrically insulated to allow simultaneous

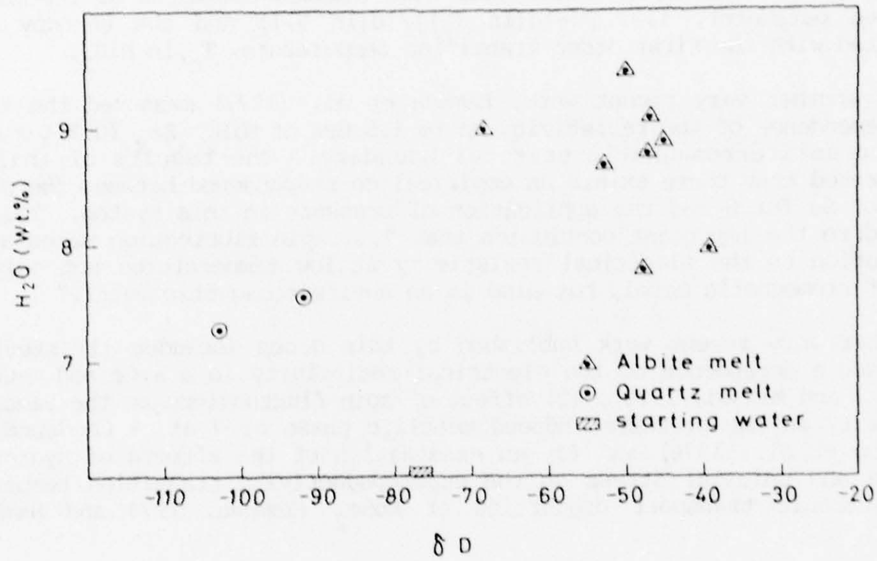

Fig. II-D-1: Plot of the D/H-ratios for synthetic quartz and albite glasses at high pressure versus their water content (from Hariya et al., 1978).

electrical resistivity measurements. The clamp cell is mounted in a He-cryostat which permits operation at temperatures down to 4.2 K (Fig. II-D-2).

With this facility, the dependence of the superconductivity transition temperature of Pb was measured against the volume change of an internal NaCl calibration sample up to 5.3 GPa. Yomo et al. (1974) also used a similar system, sans the x-ray components, to measure details of the phase diagram of Bi at reduced temperatures.

Very recently Mori and Watanabe (1978) have mounted a NiS_2 sample in a piston-cylinder apparatus and, by means of strain gauges attached to the sample, measured the pressure dependence of the paramagnetic-to-antiferromagnetic (T_n) and the antiferromagnetic-to-weak paramagnetic transition (T_c) temperatures to 1.84 GPa. These data have allowed estimates of the magnetic Grüneisen parameter, i.e., $(-[d(\ln T_n)]/[d(\ln V)])$ and the entropy change associated with the first order transition temperature, T_c, in NiS_2.

In another very recent work, Kamada et al. (1977) measured the temperature dependence of the resistivity up to 1.5 GPa of $NiS_{2-x}Se_x$ $(0.7 \leq x \leq 1.2)$ near the antiferromagnetic critical boundary. The results of this work demonstrated that there exists an empirical correspondence between the substitution of Se for S and the application of pressure in this system. This work also led to the important conclusion that "... spin fluctuation makes a large contribution to the electrical resistivity at low temperatures not only in a nearly ferromagnetic metal, but also in an antiferromagnetic metal."

Other very recent work published by this group includes (1) studies of the pressure dependence of the electrical resistivity in a α-Ce and α-Ce + 3% La (Oori and Mitsui, 1976), (2) effect of spin fluctuations on the electrical resistivity in the pressure induced metallic phase of 7 at. % Co-doped NiS_2 (Watanabe et al., 1976) and (3) an examination of the effects of hydrostatic pressure and uniaxial stress on the superconductivity transition temperature and electronic transport properties of $NbSe_2$ (Yamada, 1974 and Sambongi, 1975).

Generally speaking, the group in the Physics Department of HKU, which is involved in high pressure research, is interested in a broad spectrum of electrical and magnetic properties of solids-ranging from magnetic and superconducting phase transitions to x-ray studies of various material properties. The quality of their work continues to remain at a rather high level.

4. Research Center for Earthquake Prediciton

The Research Center for Earthquake Prediction at HKU is funded under the special R&D program of the Japanese Agency of Industrial Science and Technology to develop earthquake prediction technology. As explained by Dr. Malda, a 2500-ton press is presently under construction at HKU for the purposes of rock crushing and subsequent examination. The cost of the facility was estimated to be about ¥ 28 x 10^6 and it is expected to be available for operation in the latter part of 1978. The press is located in a new building erected expressly for the purpose of housing this facility.

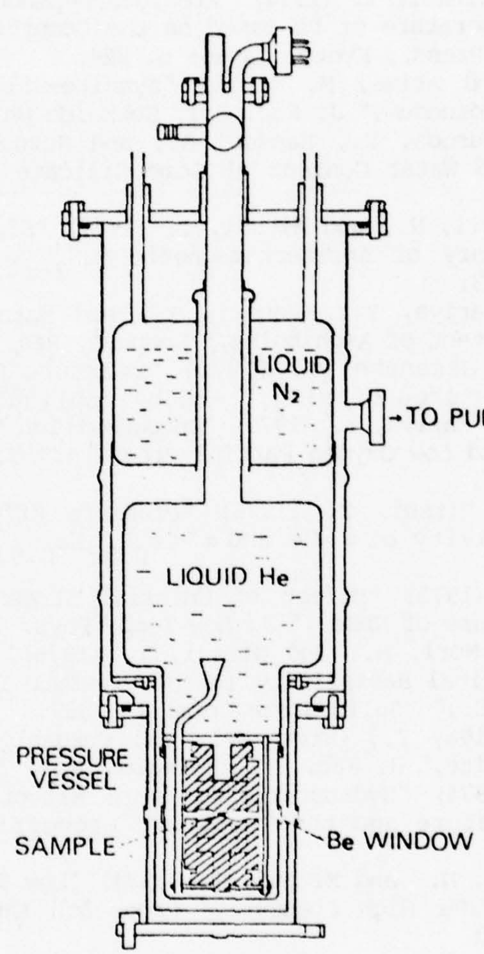

Fig. II-D-2: Internal construction of the cryostat used for high pressure x-ray studies at L-He temperatures (from Endo and Mitsui, 1974).

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E. JAPAN ATOMIC ENERGY RESEARCH INSTITUTE (JAERI)

1. Introduction

The Japanese Atomic Energy Research Institute (JAERI) was established in 1956 as the central organization in Japan responsible for the development of atomic energy for peaceful uses. The headquarters for this organization is located in Tokyo and there are JAERI facilities at Osaka, Takasaki, and Oarai; the main reactor site is found at Tokai, located northeast of Tokyo and accessible in less than two hours by train from Ueno Station in Tokyo.

Of the six reactors currently operational at JAERI, two are being used for materials research, JRR-2 and JRR-3. JRR-2 was first started-up in October 1960 and has a maximum thermal neutron flux of 2×10^{14} n cm^{-2} sec^{-1}; JRR-3 was started-up in September 1962 and has a maximum flux of 3×10^{13} n cm^{-2} sec^{-1}. Although these facilities are available for use by scientists throughout Japan, four organizations maintain research stations here for purposes of neutron scattering experiments: (1) Neutron Scattering Laboratory, Physics Division, JAERI; (2) The Institute for Solid State Physics, The University of Tokyo; (3) Department of Physics, Tohoku University; and (4) The Research Institute for Iron, Steel, and Other Metals, Tohoku University.

Two members of the resident staff at JAERI have been using high pressure techniques in their research for some time; these are Drs. Kunio Ozawa and Kazuo Gesi. Dr. Ozawa has a strong interest in pressure induced magnetic, electrical and order-disorder transitions. Much of his work is pursued in collaboration with Professor Shuichiro Anzai and his students from Keio University (cf. Part II-F-3).

2. Equipment

The high pressure research facilities of Dr. Ozawa's laboratory are quite varied: they include (1) a Be-Cu bomb for low temperature (down to liquid nitrogen) electrical measurements to 1.5 GPa; (2) a second bomb for high temperature studies to 2 GPa; (3) two optical systems equipped with sapphire windows for operation to 1.0 and 2.0 GPa; (4) a belted 400-ton press with a 4 GPa limit; and (5) a set of Bridgman anvils for use with a 200-ton press. In most all cases, manganin gauges are used for pressure measurement; hydraulic fluids in use include kerosene, normal- and iso-pentane for low temperature runs, and special silicone oil from Toshiba Co. for high temperature work. Measurement capabilities include electrical resistance, compressibility (via strain guages), DTA, and magnetic susceptibility.

3. Coupled Phase Transitions

In a very recent study, Anzai and Ozawa (1978) investigated the interesting problem of multiple phase transitions in a system linked by order parameters. In particular they studied the compound MnNiGe under pressure: this material has a first-order structural transition (Pnma-to-$P6_3/mmc$) temperature (T_D) and a second-order magnetic transition (helimagnetic-to-paramagnetic) temperature (T_N). At ambient pressure, T_D is above 370 K and T_N = 346 K; most interestingly, Anzai and Ozawa find that T_D has a negative pressure dependence whereas that of T_N is positive. They find (1) that T_D and T_N coincide at a triple point of 0.3-0.4 GPa and about 350 K, (2) that at pressures above this, T_D and T_N coincide and; (3) that the pressure slope of the (T_D T_N)-line above the triple point is intermediate to the values of dT_N/dP and dT_D/dP. (See Fig. II-E-1). They report that this is the first example of a collaborating phase transition in which two distinctly different physical properties can cause a simultaneous phase transition. They propose a mechanism for the transition and further analyze it in terms of the Landau-theory of phase transitions. Details of some of Dr. Ozawa's other collaborative research efforts with Professor Anzai are reviewed in Part II-F.

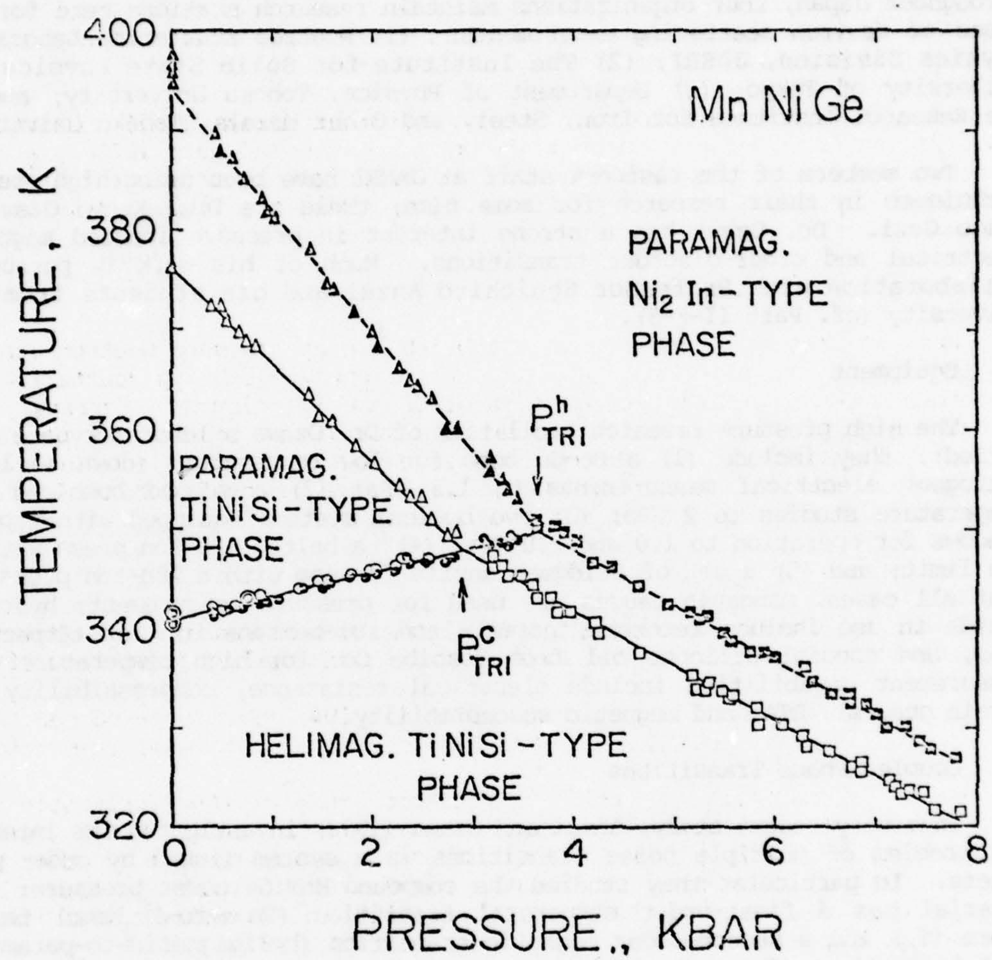

Fig. II-E-1: Pressure - temperature phase diagram of the helimagnetic TiNiSi-, paramagnetic TiNiSi-, and paramagnetic Ni_2*In*-type phases in MnNiGe. Closed and open symbols represent heating and cooling runs, respectively. The triple point is determined to be 360 MPa on heating and 290 MPa on cooling (from Anzai and Ozawa, 1978).

4. Ferroelectric Phase Transitions

Another active high pressure research program at JAERI is focused on the characterization and understanding of phase transitions in dielectric materials. Very recently Gesi et al. (1978) have measured the phase diagram of $(ND_4)_3D(SO_4)_2$ to 0.9 GPa and -110 C, while Gesi and Ozawa (1978 and 1977) have examined the effect of hydrostatic pressure on the phase transitions in CsH_2PO_4 (and CsD_2PO_4) and $SnCl_2$-$2H_2O$, respectively.

In another very interesting study, Gesi and Ozawa (1976) found, from their dielectric constant measurements on triglycine selenate (TGSe), a change in the transition orders: at elevated pressures, the ferroelectric transition in TGSe changes from second- to first-order. This transition point has been denoted the Curie-critical point.

5. Neutron Scattering Studies

Work is presently underway to establish a high pressure neutron scattering facility. The objective initially is to carry out Bragg scattering measurements using standard neutron time-of-flight techniques. Currently different types of high pressure containers are being tested, in particular Be-Cu, Ti-Zr and Al_2O_3. Tests on both Fe and NaCl samples are underway by Professor Kamigaki of Tohoku University and Dr. Sakimoto of JAERI. Studies on ice VI and VII are planned for the immediate future.

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F. KEIO UNIVERSITY (KOU)

1. Introduction

Keio University (KOU) or Keio-gijuku is the oldest modern, higher education institution in Japan. Yukichi Fukuzawa established Rangaku-sho (Institute of Dutch Learning), as it was originally known, in the winter of 1858

with the objective of teaching Dutch to young men of the Okudaira clan. Today the school has four campuses, two in Tokyo and two in Yokohama. High pressure facilities are located in the Departments of Mechanical Engineering and Applied Chemistry on the Yagami Campus in Hiyoshi, Yokohama.

2. Department of Mechanical Engineering

High pressure studies in the Department of Mechanical Engineering are directed toward the general characterization and understanding of the thermodynamical properties of fluids. Research in this area is primarily under the leadership of Professor Koichi Watanabe, who recently completed an excellent review of all thermodynamical properties research in Japan (Watanabe, 1977). Studies are currently underway on the following systems under the guidance of Professor Masahiko Uematsu: various refrigerants, water, and CO_2. P-V-T studies have been, and continue to be, pursued on many commonly used refrigeration fluids; a number of these are supplied to KOU by E. I. duPont Co.

Using a dead-weight piston gauge, the density of C_2F_6 (refrigerant #R116) is being measured in the temperature range from -85 to +95 C and at pressures up to 9 MPa. Concurrent experiments on the same material are designed to provide information on the coexistence of two phases of C_2F_6 along the saturation curve. These measurements are carried out over the temperature range from 17 to 20 C and in the density range from 0.4 to 0.84 gm/cm^3. Moreover, measurements are underway of the compressibility of an azeotropic mixture of $CHClF_2$ (R22) and C_2ClF_5 (R115); the mixture is identified as R502. The second virial coefficient of R502 will be determined from these compressibility data up to 15 MPa and in the temperature range from 0 to 130 C. The purpose of this work is to provide new and more reliable thermodynamical data on various refrigerants which either are, or may be, used in actual refrigeration applications.

Previously published P-V-T data on water from KOU have spanned the (P,T)-range up to 200 MPa and from 323.15 to 773.15 K, respectively. Current studies are being extended up to 1000 C and to 1 GPa through analysis of published data. The objectives of this work are (1) to provide a critical evaluation of the data in the literature which, when combined with KOU data, will yield a set of reliable thermodynamic P-V-T coordinates and (2) to estimate surface state corrections in the P-V-T range.

Using a flow calorimeter designed and built by this group, the isobaric specific heat capacity of CO_2-vapor has been measured in the (P,T)-range up to 1 MPa and from 0 to 130 C; current plans are to extend these measurements to 5 MPa.

The high rate of publication, e.g., fifteen papers in 1976 and 1977, speaks well for the productivity of the group and, from all indications, the high quality and progress of the group will continue.

3. Department of Applied Chemistry

The second group involved in high pressure research at KOU is under the

general direction of Professor Tetsuro Yoshida in the Department of Applied Chemistry. Many of the recent studies are under the immediate supervision of Professor Shuichiro Anzai, who publishes extensively with Dr. Kunio Ozawa of the Japan Atomic Energy Research Institute (cf. Part II-E). This group has performed pressure dependent measurements of structural, electrical, and magnetic properties of a wide variety of solids, viz., NiS (Anzai and Ozawa, 1968, 1974, 1977); Cr_3Te_4 (Ozawa et al., 1970); $NiTi_2S_4$ (Anzai and Ozawa, 1973); FeS_{1+x} and Fe_3Se_4 (Ozawa and Anzai, 1974).

The first study of NiS was performed in a 2%-BeCu alloy pressure vessel where hydraulic pressures up to 1.5 GPa could be achieved. By means of cryogenic cooling and electrical heating, the temperature in the pressure bomb could be continuously varied from L-N_2 to about 320 K. High pressure data were obtained from four-probe resistance measurements. The objective of this experiment was to carry out the first measurement at elevated pressures of the first-order, antiferromagnetic transition in NiS. It was found that (1) this magnetic transition is also reflected by an abrupt change in the electrical resistivity, similar to a semiconductive-metallic transition, and (2) the transition temperature (230 K at ambient pressure) is depressed linearly to about 190 K and 0.7 GPa. In discussing these results, considerations are given to the d-band electronic energy states and their effects on the stability of the structure.

A magnetic induction system was added to these high pressure facilities to permit simultaneous magnetic susceptibility measurement capabilities. The pressure dependence of the Curie temperature and an anomaly in the electrical resistivity were measured in Cr_3Te_4 samples containing magnetic atom vacancies with this system. The results are discussed in terms of magnetic exchange interactions and comparisons with structurally similar systems (Ozawa et al., 1970).

Based on similar high pressure electrical resistivity measurements, this group at KOU found the order-disorder transition in $NiTi_2Si_4$, also with magnetic atom vacancies, to be a first-order transition. The pressure dependence of the transition temperature was measured up to 0.7 GPa and the results are rigorously analyzed in terms of vacancy coordination, order-disorder states, and electron screening effects (Anzai and Ozawa, 1973).

Further excellent studies of magnetic phase transitions have been carried out on the pressure dependence of the Néel and ferrimagnetic Curie temperatures in FeS_{1+x} ($0 \geq x \geq 0.12$) and Fe_3Se_4. In this study the aforementioned high pressure resistivity measurements were coupled with strain-gauge expansion data. Also, as in the previous studies by this group, the experimental results are discussed in terms of their theoretical consequences, in this case, through comparisons with transitions in similar magnetic structures. It was found that a simple correlation can be used between the sign of exchange strictions and the number of 3d-electrons on the metal atoms in NiAs-type compounds (Ozawa et al., 1973 and Ozawa and Anzai, 1974).

By combining recent strain-gauge measurements on NiS with their previous electrical resistance data, Anzai and Ozawa (1977c) have formulated a more

detailed analysis of this system. The linear expansivity data have allowed evaluation of the volume dependence of the resistivity and this information has been incorporated into calculations based on an existing model (Lidiard model) for an itinerant antiferromagnet to explain both the pressure dependence and the metal-nonmetal transition and its first-order characteristics. This is reported as being the first attempt to estimate the energetics for this transition in NiS.

In one of their most recent studies, Ozawa and Anzai (1977) have measured the effect of pressure on a new magnetic transition temperature in the ferrimagnetic state of $Mn_{1.77}Sn$. They find that this new transition can be explained by a change in the electron-lattice cross section due to atomic clustering accompanied by spin flipping below the transition temperature.

4. Summary

Although high pressure research at KOU does not appear to have changed significantly in recent years, the quality of the research remains at a very high level. The primary interests of the group in the Department of Mechanical Engineering are clearly focused on the characterization of the thermodynamical properties of fluids while those in the Department of Applied Chemistry are concerned with various transitions in magnetic materials. Each study of the latter group is usually concluded with a rather in-depth analysis of the data in terms of existing theories with the fundamental objective of gaining further understanding of the appropriate transition mechanisms.

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G. KOBE STEEL, LTD. (KSL)

1. Introduction

Kobe Steel, Ltd., (KSL) is located in the heart of Kobe at the base of Mt. Rokko on the Osaka Bay; as a matter of fact some of the land presently being utilized by KSL has actually been reclaimed from the Bay. KSL has long been a major supplier of high pressure research equipment in Japan and it is fitting that a fundamental research program involving high pressure techniques should be underway here. The high pressure research activities of KSL are pursued within the Asada Fundamental Research Laboratory (AFRL).

AFRL was founded on October 1st, 1964, and named in honor of its director, Dr. Tsunesaburo Asada, Professor Emeritus of Osaka University. The research goals of AFRL are aimed toward the solution of scientific problems with very long range objectives or, as phrased in the literature of KSL: "Asada Fundamental Research Laboratory ... places special emphasis on research of long-range significance - the pursuit of scientific knowledge in advance of needs for specific applications and technology of the decades ahead."

A rather broad field of physical science is covered at AFRL: in addition to high pressure physics, their activities include low temperature physics, ocean development studies, and pollution control. Needless to say, the Laboratory maintains a wide selection of modern and sophisticated research equipment including a mass spectrometer, electron probe microanalyzer, 70 KG-superconducting magnet, He liquifier, and various metals processing instruments.

2. *High Pressure Equipment*

There are two main pieces of high pressure research equipment currently in use at AFRL, each a cubic anvil apparatus of the type "... originally developed by Kobe Steel." Basically the cubic press is a rather straightforward device: six segments of a cube are uniformly driven together compressing the central cubical cavity. The compressional load from an external, uniaxial press is delivered to the upper and lower cubic segments directly. The four lateral pieces are each provided with 45^{o} surfaces on top and bottom, thus the vertical load is redirected horizontally. Because of this 45^{o} taper, the resulting centrally directed force components on all six cubic faces are essentially the same during operation.

The smaller of the two hydraulic presses in use at AFRL has a load capability of 200 tons, the larger, 2500 tons. This latter unit is used to compress a 20 mm cube, thus providing an 8 cm^3 high pressure volume; it has an upper pressure limit of about 4 GPa. Graphite low resistance heaters permit operation of sustained temperatures to 2000 C or flash heating in the 3000 to 4000 C ran[illegible]. The other system is designed to operate on a 6 mm cubic apparatus and [illegible]roduce pressures and temperatures up to 10 GPa and 1000 C, respectively. [illegible]se systems were completed over ten years ago and today are used for rese[illegible] studies on the synthesis of super-hard materials, in particular as relate[illegible]o the kinetics of phase transformations.

An energy dispersive x-ray detection system is also in use with one of the presses; the details of this are discussed below.

3. Super-Hard Materials Development

High pressure research activities at AFRL today appear to be focused mainly on super-hard materials. This group is involved in the national super-hard materials program discussed in Appendix A and, in that context, work is underway here on in situ sintering conditions for both diamond and boron nitride (BN). These efforts represent perhaps one of the first attempts to study structural properties under conditions of elevated pressure and temperature.

One of the most interesting results obtained to date, and one which is not yet understood, is the observation of graphite formation in a (P, T) range where the diamond structure is stable. X-ray energy spectra of $1/2\mu$ to 1μ -diamond powder recorded by Inoue (1978) are shown in Fig. II-G-1; these curves were recorded at 7.5 GPa and 20 C (lower), 7.5 GPa and 1300 C (middle), and ambient conditions (upper). The formation of graphite is evidenced by the appearance of the graphite (002)-peak on the middle curve. The causes of this conversion of diamond to graphite are presently under investigation. It is possible that, because of the extreme hardness of the diamond, the externally measured pressure of 7.5 GPa may not be uniformly distributed throughout the reaction chamber. If the actual contact pressure on portions of the diamond surfaces were somewhat less than this, diamond-to-graphite conversion would be expected. Inoue (1978) reports that the compressive strength of their diamond compacts is in the 4 to 5 GPa range, but that the material lacks toughness. (It is noted that these compacts are made without the use of a binder.) Another problem currently under examination here is why the compressive strength is limited to 5 GPa and what, if any, are the effects of the residual pressure limit.

Similar studies are also underway on BN. In Fig. II-G-2, Inoue's (1978) most recent in situ x-ray data on this system are shown. The conversion of BN from the hexagonal to the cubic structure between 1000 and 1300 C is clearly evidenced in the upper two curves. These data were recorded in a 2-to-4 hour period from a cylindrical sample approximately 3 mm in diameter. Research on the formation of cubic-BN continues along with the diamond studies, in addition to work on other high strength steels.

4. Energy Dispersive X-Ray Analysis

a. Introduction

Dr. Katsuhiko Inoue has set up a solid state x-ray detection system on the 6 mm-cubic press; he has carried out extensive developments and analyses of this facility as part of his doctoral thesis under Professor Syun-iti Akimoto of the University of Tokyo. Unfortunately, the greater part of the details of his thesis have not been published (Inoue, 1975) and for this reason, an effort will be made to summarize some of the more important features of the work here. The thesis itself is divided into five parts: Part I

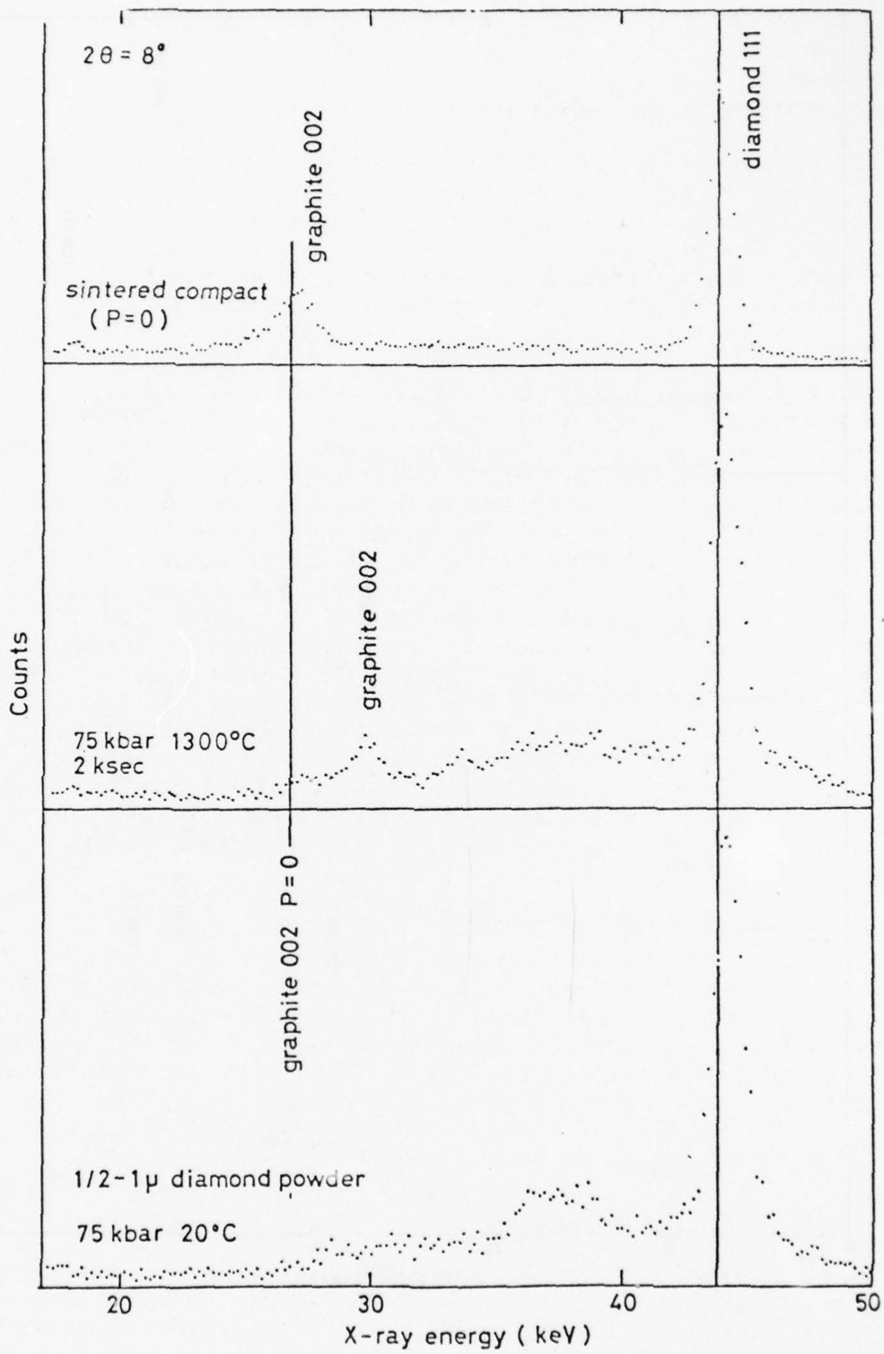

Fig. II-G-1: In situ high pressure - high temperature x-ray energy spectra of carbon (from Inoue, 1978).

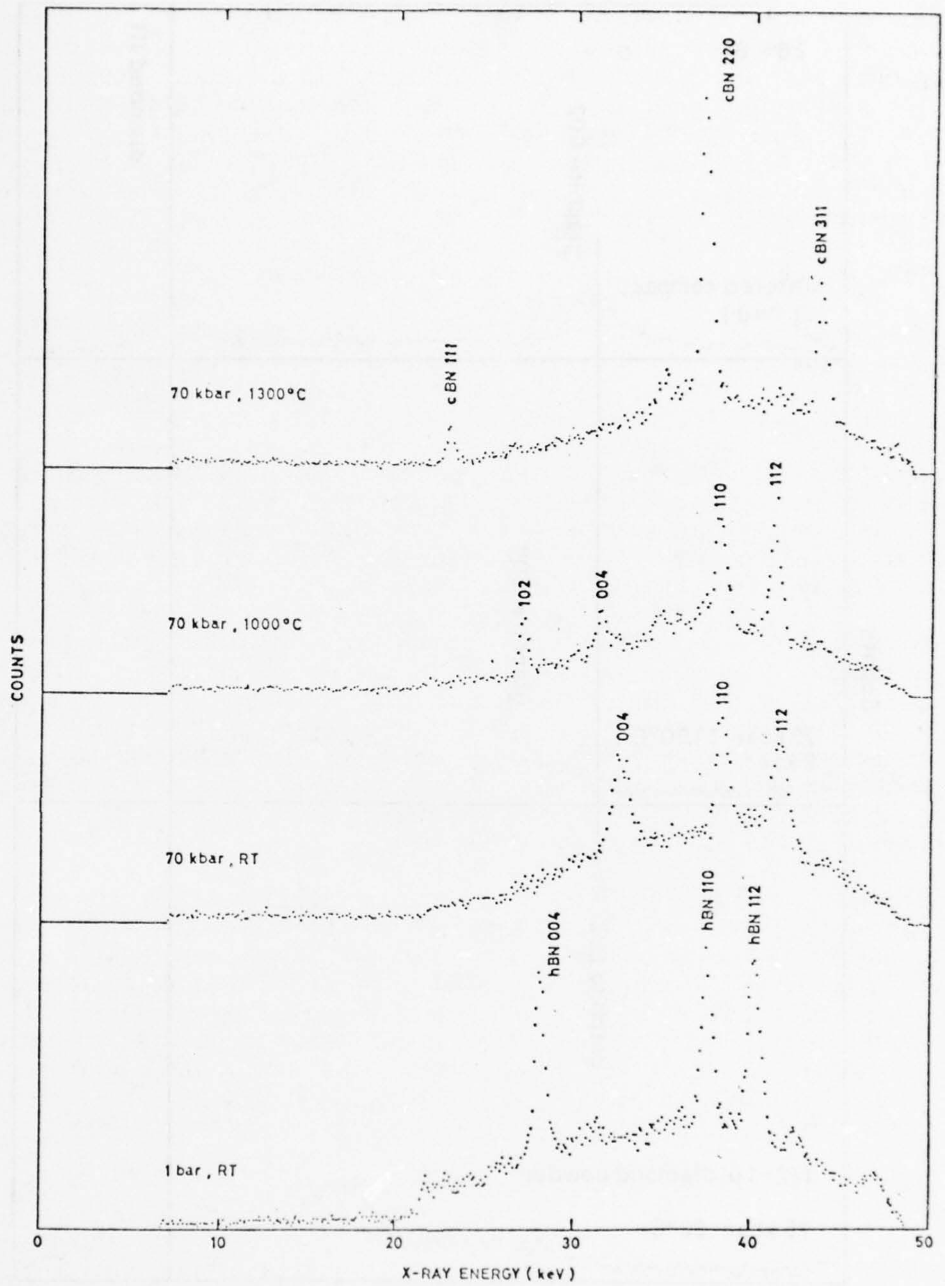

Fig. II-G-2: In situ high pressure - high temperature x-ray energy pectra of boron nitride (from Inoue, 1978).

is concerned with the details of the energy dispersive system; Part II addresses the difficult problem of interpreting the intensities of the x-ray energy data for the purposes of crystallographic structure determination; in Part III a suggestion is made to establish the melting curve of Pb as a high pressure/high temperature calibrant and careful measurements of this melting curve are included to 9 GPa; the last two parts are devoted to measurements of the wurtzite-rocksalt transition in ZnO (Part IV) and the olivine-spinel transition in Fe_3SiO_4 (Part V).

b. Description of System and Evaluation of Accuracy

The energy dispersive system used by Inoue consists of a Li-drifted Ge detector, a 1024-channel analyzer, plus associated electronics. Polychromatic x-radiation from a W-target x-ray tube enters through one vertical edge of the cubic press; the scattered radiation is analyzed through the diagonally opposite edge, providing an angular window of $\pm 35^\circ$ in 2θ. Significant background contributions to the measured spectrum are minimized by employing a very fine collimation system: the receiving collimator, which is 0.4 mm wide and 300 mm long, provides a 2θ-window only 0.053°-wide. The measured energy spectrum is analyzed by a non-linear least-squares fitting routine based on the Gauss-Seidel iteration method.

To assess the accuracy of the system, NaCl was examined up to 7.2 GPa. The measured diffraction pattern at this pressure includes 12 peaks ranging from the (220) to the (642) reflections (Fig. II-G-3). Based on a comparison of the ten best peaks at ambient and elevated pressures, the shift in the NaCl lattice parameter is estimated to an accuracy of 0.012% and this, combined with Decker's (1971) equation of state calculations, leads to an uncertainty in the pressure of ± 0.016 GPa at 7.240 GPa, or about ± 0.2%. (This ignores the uncertainty in the equation of state calculation itself.)

Detailed considerations are given to the resolution of the energy dispersive system as compared with conventional angular diffractometry, e.g., using Mo $K\alpha$ radiation, the conclusion is reached that for high pressure studies the energy dispersive system yields "... more accurate determination of lattice parameters of substances at high pressure than the conventional angular dispersive technique." (Inoue, (1975)) It is the opinion of this author that the statement should be restricted to the cubic-anvil apparatus, i.e., there are other high pressure x-ray diffraction experiments where conventional x-ray measurements techniques may prove to be more accurate.

c. High Pressure X-Ray Energy Intensity Analyses

The problem of structural determination based on energy dispersive x-ray intensity data is rather complicated for several reasons: firstly, both the incident beam and the quantum counting efficiency of the detector have very distinct and often complex energy profiles and secondly, the response of the sample will also be energy dependent. However, Inoue (1975) has considered these problems and, in so doing, analyzed ambient pressure structural information for Fe and W, and the high pressure (B2) structure of KCl. Generally he reports R-factors of less than 10%.

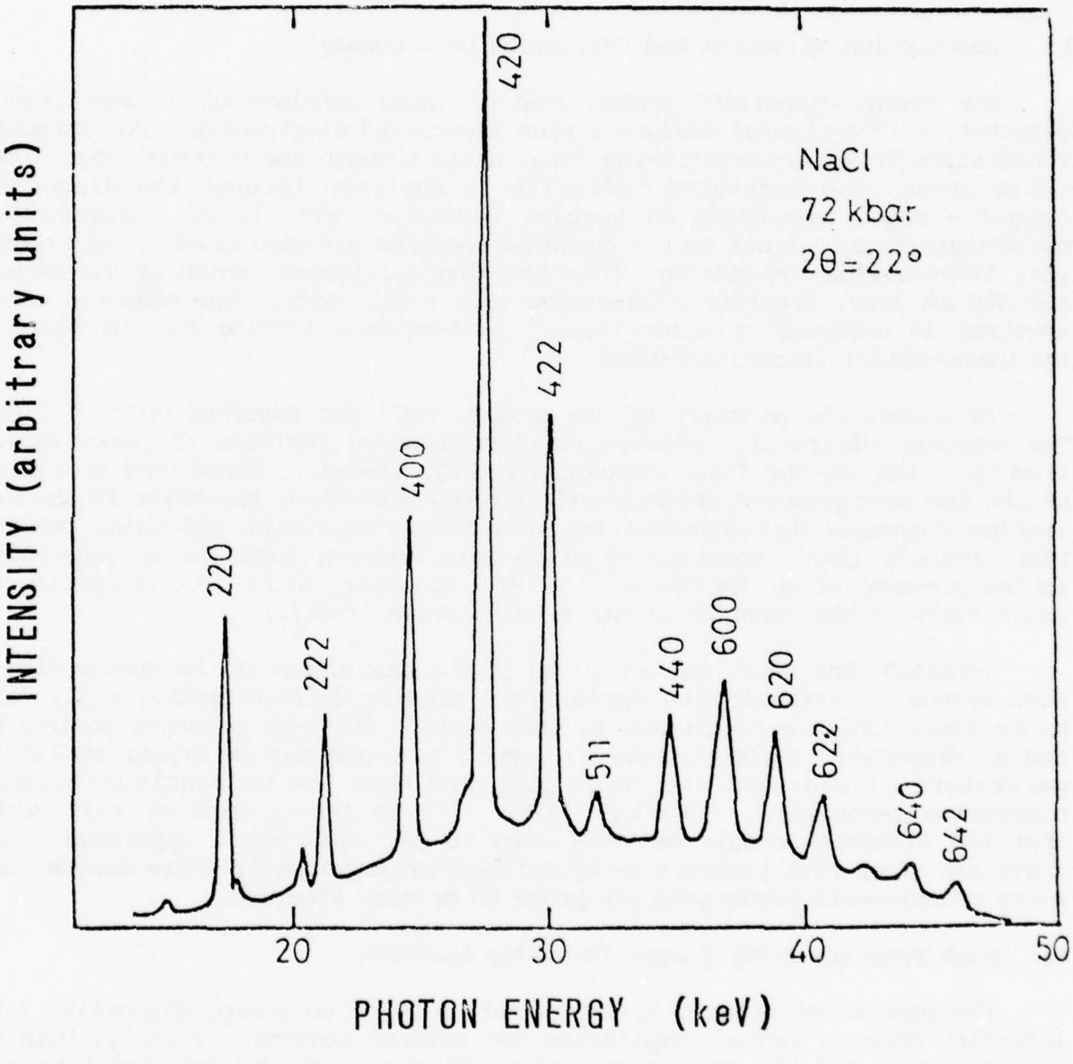

Fig. II-G-3: Energy dispersive x-ray diffraction pattern for NaCl at about 7.2 GPa (from Inoue, 1978).

The overall conclusion however, is that considerable work is still required before the quality of energy dispersive structural analyses will surpass the highly refined angular dispersive techniques. Inoue suggests that, before energy dispersive x-ray intensity data can be used for purposes of crystallographic structural analyses, much more detailed information is needed in the following areas: (1) the energy spectrum of various types of x-ray tubes, including the spectral dependence on the operating power; (2) the energy and intensity dependence of the quantum counting efficiency of the detector; and (3) the energy dependence of the material absorption coefficients, especially in the vicinity of an absorption edge.

d. Melting Curve of Lead to 9 GPa

Inoue (1975) finds that useful high pressure energy dispersive x-ray data can be obtained despite the presence of a pyrophyllite gasket. Consequently, x-ray measurements can also be carried out to temperatures of about 1500 C. (It should be noted here that a rotating anode x-ray tube is employed in this application. Consequently, the tube may be operated at up to 10 times the conventional power limit.) With regard to the hold time in the cubic press at elevated temperatures, based on in situ measurements on NaCl, Inoue reports a monotonically increasing decrease in the set pressure with increased temperature, amounting to 20% decrease at 6 GPa and 1400 C. The effects of temperature cycling are also considered in some detail.

It is suggested by Inoue (1975) that the melting curve of Pb would serve as an excellent pressure calibrant for high pressure/high temperature studies. With this end in mind, he has measured the melting temperature of Pb up to 9 GPa (as measured against the NaCl-pressure scale (Decker, 1971)). His results are reproduced in Fig. II-G-4.

e. High Pressure Studies of ZnO and Fe_2SiO_4

In the fourth and fifth parts of his thesis, Inoue (1975) presents data on the wurtzite-to-rocksalt transition in ZnO up to 8.5 GPa and 1200 C and the olivine-to-spinel transition in Fe_2SiO_4 up to about 6 GPa and over the temperature range from 600 to 1200 C. In the case of ZnO, the phase boundary is approximately expressed by the relation:

$$P = 8.0277-0.0023T$$

where T is in Kelvins and P in GPa; the Fe_2SiO_4 phase boundary is similarly expressed by a linear function:

$$P = 2.7775-0.0025T$$

in the same units. Previous high pressure structural investigations of these minerals have been based on data recorded from quenched samples. In both cases, significant differences are found to exist between the in situ and quenched-sample phase diagrams. In the case of Fe_2SiO_4, about a 20% increase in the transformation pressure is found in the in situ data, although the P-T slope is the same for each measurement (Fig. II-G-5). However, for ZnO,

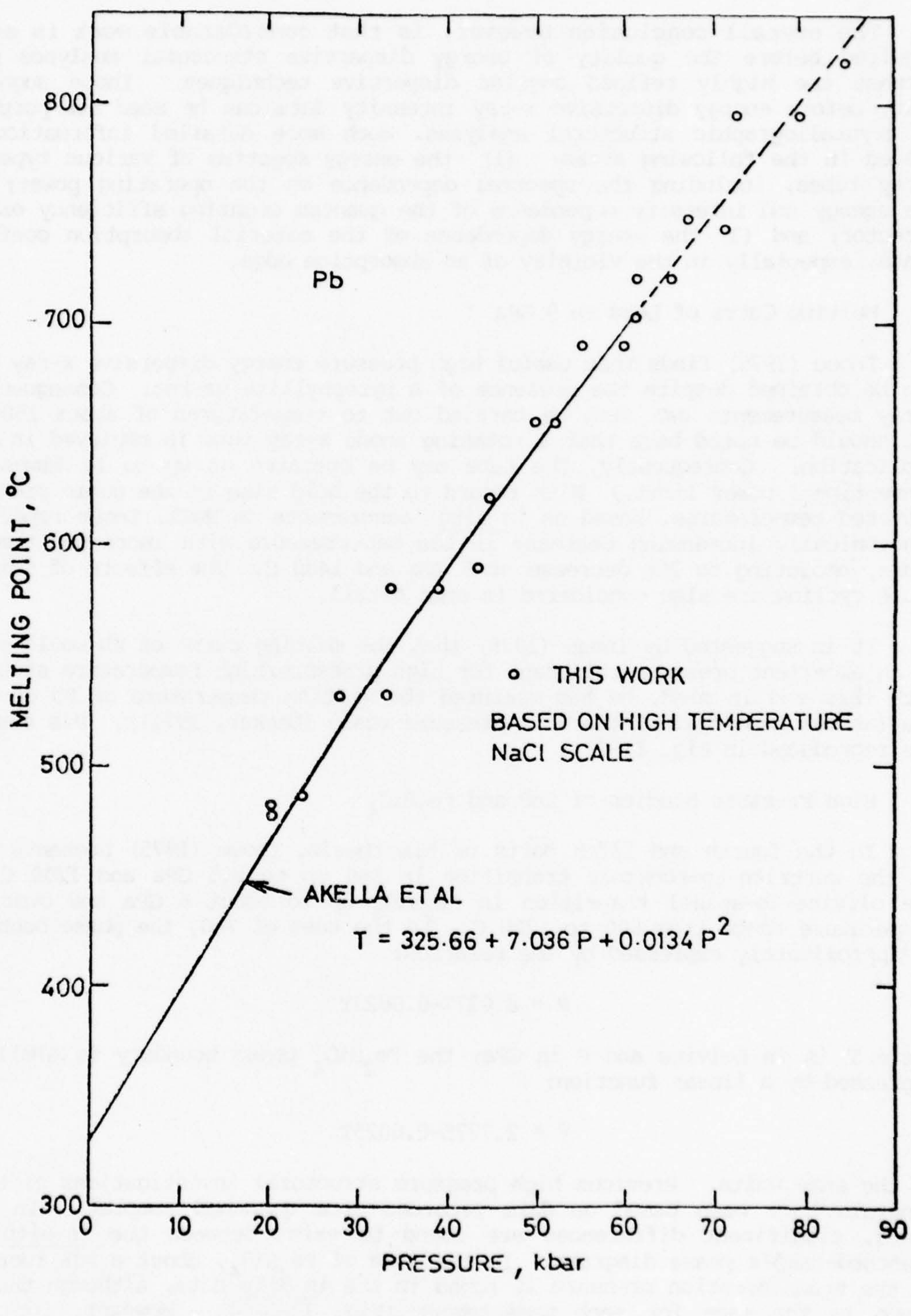

Fig. II-G-4: Melting curve of Pb based on the NaCl pressure scale (from Inoue, 1975).

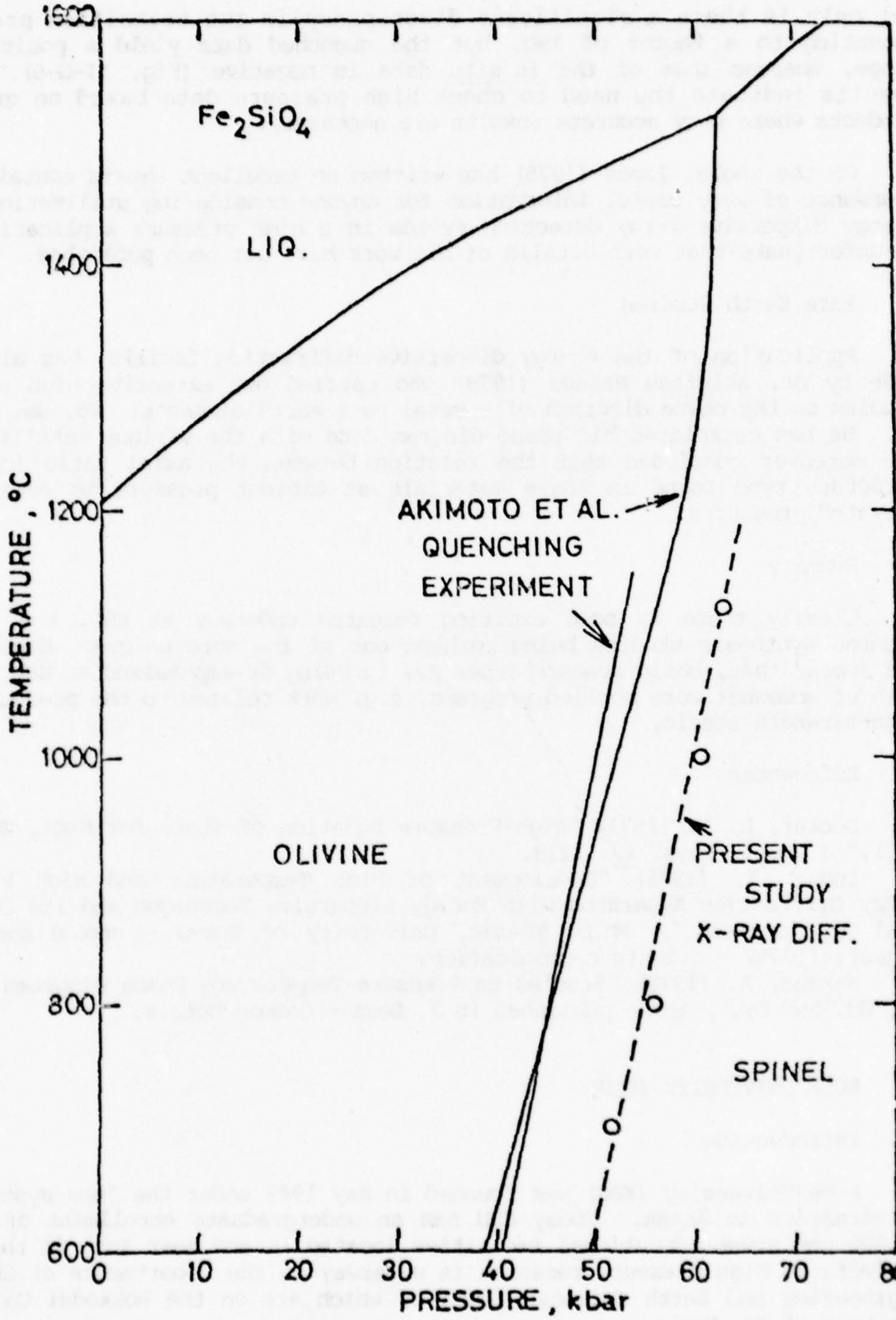

Fig. II-G-5: Olivine-spinel transition curve based on <u>in situ</u> NaCl pressure calibration (from Inoue, 1975).

not only is there a significant discrepancy in the transition pressure, amounting to a factor of two, but the quenched data yield a positive T-P slope, whereas that of the in situ data is negative (Fig. II-G-6). These results indicate the need to check high pressure data based on quenched products where very accurate results are necessary.

On the whole, Inoue (1975) has written an excellent thesis containing an abundance of very useful information for anyone considering utilization of an energy dispersive x-ray detection system in a high pressure application. It is unfortunate that more details of his work have not been published.

5. Rare Earth Studies

Application of the energy dispersive diffraction facility has also been made by Dr. Akimitsu Nakaue (1978) who carried out extensive high pressure studies on the phase diagrams of several rare earth elements: Nd, Sm, Gd, and Dy. He has correlated his phase diagram data with the various metallic radii and moreover concluded that the relation between the axial ratio (c/a) and structure type found in these materials at ambient pressure is retained at elevated pressures.

6. Summary

Clearly there is some exciting research underway at KSL, the in situ diamond synthesis studies being perhaps one of the more unique. However, it did appear that, basic research, per se, is being de-emphasized at KSL for the sake of somewhat more applied programs, e.g. work related to the production of high-strength steels.

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H. KOBE UNIVERSITY (KBU)

1.. Introduction

Kobe University (KBU) was founded in May 1949 under the "new-system" for universities in Japan. Today KBU has an undergraduate enrollment of almost 10,000 and seven educational facilities located in and near Kobe in the Hyogo Prefecture. High pressure research is underway in the Departments of Chemical Engineering and Earth Sciences, both of which are on the Rokkodai Campus at the base of Mt. Rokko.

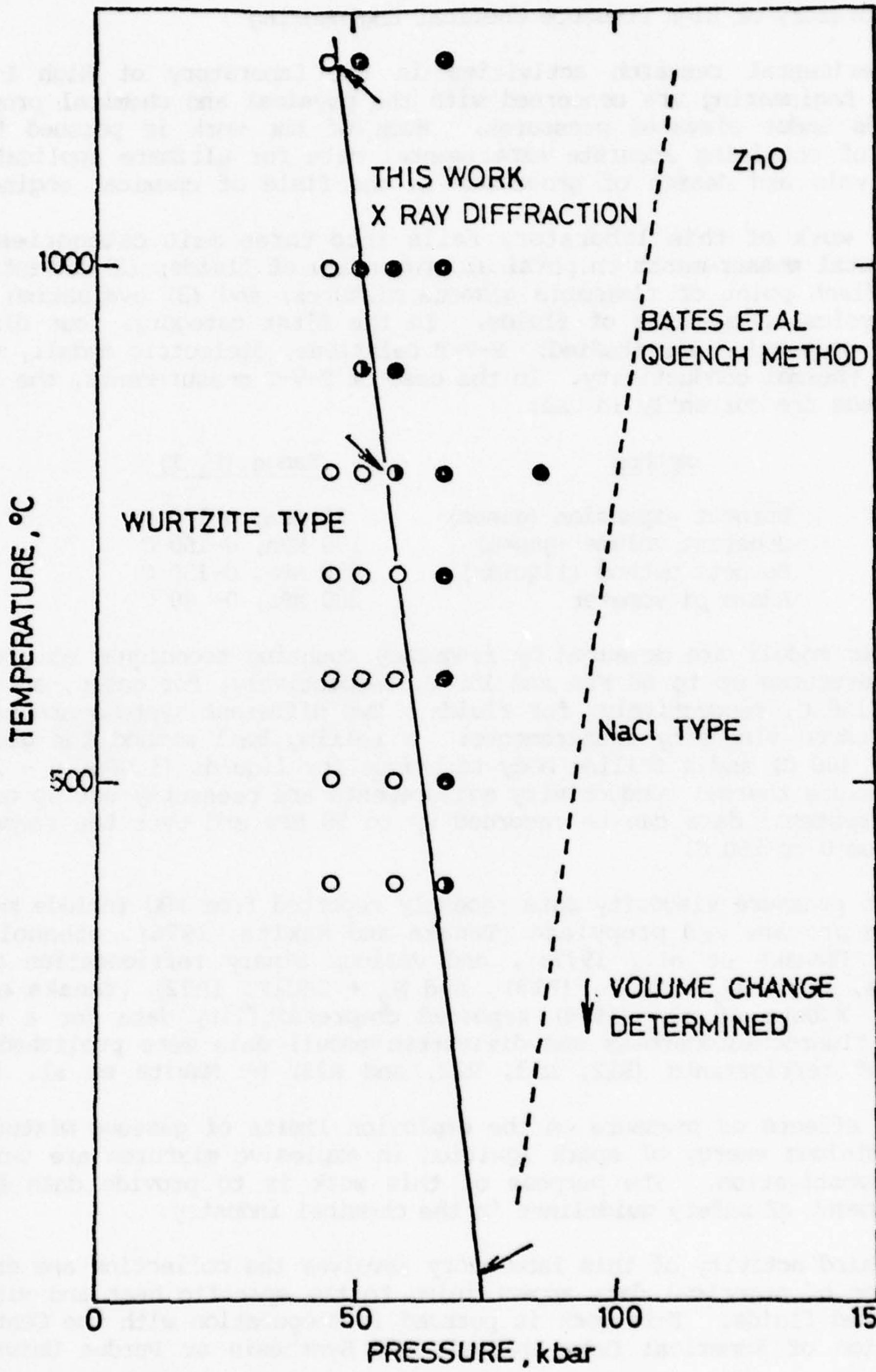

Fig. II-G-6: Phase diagram of ZnO based on in situ NaCl pressure calibration (from Inoue, 1975).

2. Laboratory of High Pressure Chemical Engineering

Experimental research activities in the Laboratory of High Pressure Chemical Engineering are concerned with the physical and chemical properties of fluids under elevated pressures. Much of the work is pursued for the purpose of obtaining accurate experimental data for ultimate application in the analysis and design of processes in the field of chemical engineering.

The work of this laboratory falls into three main categories: (1) experimental measurements on physical properties of fluids; (2) investigation of the flash point of flammable gaseous mixtures; and (3) evaluation of the thermophysical properties of fluids. In the first category, four different physical properties are studied: P-V-T relations, dielectric moduli, viscosity, and thermal conductivity. In the case of P-V-T measurements, the following methods are currently in use:

Method	Range (P, T)
Burnett expansion (gases)	20 MPa, 0-150 C
constant volume (gases)	100 MPa, 0-150 C
Burnett method (liquids)	500 MPa, 0-150 C
Adams piezometer	200 MPa, 0- 80 C

Dielectric moduli are measured by frequency counting techniques at pressures and temperatures up to 50 MPa and 150 C, respectively, for gases, and to 300 MPa and 150 C, respectively, for fluids. Two different systems are used for high pressure viscosity measurements: a rolling ball method for gases (10 MPa; 0 - 100 C) and a falling body technique for liquids (1 GPa; 0 - 200 C). High pressure thermal conductivity measurements are presently set up only for gaseous systems; data can be recorded up to 50 MPa and over the temperature range from 0 to 150 C.

High pressure viscosity data recently reported from KBU include measurements on propane and propylene (Tanaka and Makita, 1976), ethanol-water mixtures (Tanaka et al., 1977a), and various binary refrigeration gaseous mixtures, e.g., N_2 + $CClF_3$ (R13), and N_2 + $CHClF_2$ (R22) (Tanaka et al., 1977b). Kubota et al. (1974) reported compressibility data for a collection of fluorochlorocarbons and dielectric moduli data were published for a series of refrigerants (R12, R13, R22, and R23) by Makita et al. (1977).

The effects of pressure on the explosion limits of gaseous mixtures and on the minimum energy of spark ignition in explosive mixtures are currently under investigation. The purpose of this work is to provide data for the establishment of safety guidelines in the chemical industry.

A third activity of this laboratory involves the collection and critical evaluation of numerical data appertaining to the specific heat and viscosity on selected fluids. This work is pursued in cooperation with the Center for Information of Numerical Data Analysis and Synthesis at Purdue University.

3. Department of Earth Sciences

Dr. Keisuke Ito, who until recently had been working in Professor Kawai's laboratory in nearby Osaka University, is one of the leading high pressure researchers in the Department of Earth Sciences at KBU. Research interests here, of course, are centered around materials of geophysical interest. In pursuit of ultra-high pressure data, quite recently a triple-stage press was built using a sintered diamond as the last-stage piston (Ito and Endo, 1977). Actually the split sphere apparatus in use at Osaka University constitutes the first two stages of this system. This third stage consists of a pyrophyllite octahedral chamber designed for compression in the split-sphere apparatus. In the pyrophyllite plug are contained two opposed anvils; the surrounding pyrophyllite is designed to provide lateral support for the anvils and serve as a pressure gasket.

Initial studies were carried out using two cemented WC-anvils to produce pressures over 22 GPa with about 100 tons of ram load. In a second experiment, one of the WC-anvils was replaced with a sintered diamond anvil made by Ito, O'Mara, and Kennedy at UCLA. In this case, almost a four-fold increase in performance was realized, i.e., the same pressure, as measured by the electrical transition in GaP, was achieved with approximately 1/4 the ram load. In the latter run, some deformation was produced in the remaining WC-anvil. Work is now planned to grow sintered diamond compacts at KBU and ultimately run this system with two opposed sintered diamond anvils.

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I. KYOTO INSTITUTE OF TECHNOLOGY (KIT)

1. Introduction

Kyoto Institute of Technology (KIT) is located in the heart of Kyoto, about a 10-minute taxi ride from the main Shinkansen station. Several groups

at KIT are involved in high pressure research, most of which are located in the Department of Chemistry under Professors Taisuke Ito, Hiroshi Teranishi, and Tatsuo Minamiyama. In addition, some pressure related research is also pursued under Professor Masanori Sato in the Faculty of Textile Science.

2. Department of Chemistry

a. Polymer Studies

Professor Ito runs a very neat and well organized laboratory dedicated to the study of the effects of pressure on polymers and related compounds. The group uses primarily a piston-cylinder apparatus equipped with a Be window for x-ray diffraction studies (Ito and Marui, 1971). The pressure is measured with a controlled-clearance piston gauge which is calibrated annually at Kobe Steel, Ltd. The estimated uncertainty in the measured pressure in less than $\pm$0.015% at about 1 GPa.

The pressure cell is used on a rather unique moving film x-ray camera which permits up to 15 separate exposures on a single film (Ito, 1974a). The procedure is to expose each position at a different fixed pressure; the processed film can then be analyzed in terms of pressure induced structural changes in the sample.

One material examined in this system is adamantane. Based on careful high pressure x-ray measurements, Ito (1973) has found that at about 480 MPa, adamantane undergoes a structural transition from face-centered cubic to tetragonal and, based on the intensity data, the tetragonal structure is presumed to be the same as a previously reported high temperature form.

Ito (1974b) has also carried out studies on the compressibilities of polypropylene and polyoxymethylene. Generally he finds that under hydrostatic pressure, these polymer crystals strain predominantly in a direction normal to the fiber axis. This is so even in cases where the elastic moduli parallel to the fiber axes are small, due to the helical structure of the polymer chain.

b. Liquid Studies

The group in Professor Teranishi's laboratory is involved in a number of different high pressure measurements on fluids. These include ultrasonic velocities, refractive indices, and chemical reaction rates.

The ultrasonic measurements are performed using a pulse technique at frequencies up to 1 MHz in a pressure, temperature range to 210 MPa and from 10 to 60 C, respectively. Studies were recently concluded of the pressure dependence of the density of n-hexane, n-heptane, and n-octane (Takagi, 1978).

Another system has been set up in this laboratory using a pressure bomb equipped with quartz windows for optical studies to 50 MPa. The system is operated in conjunction with an He-Ne laser and a standard interferometer. Initial results have been reported on the pressure dependence of the refractive indices of CCl_4, C_6H_6, C_6H_5Cl, and $C_6H_5NO_2$ (Takagi and Teranishi, 1977).

In addition to the above, this group is involved in studies of chemical reaction rates to about 9 MPa. The results of an investigation of the kinetics of addition reactions of CO with organic compounds in hydroiodic acid were recently reported by Teranishi et al. (1976 and 1977).

c. Thermal Conductivity of Water

A third group in the Chemistry Department at KIT directed by Professor Minamiyama is involved in very accurate measurements of the thermal conductivity of water. Using a new cell constructed expressly for this purpose, thermal conductivity data have recently been reported in the pressure, temperature range: 9.8 - 147.0 MPa, 104 - 420 C, respectively. The accuracy is estimated to be within 1.7% below 400 C and within 2 - 2.5% above 400 C. The results below 50 MPa are in good agreement with previously published data, however, the results above 100 MPa are in serious disagreement with published work (Yata et al., 1978a and b).

3. Faculty of Textile Science

Professor Sato's laboratory, in the Faculty of Textile Science, is involved, inter alia, with the study of electrochemical reactions as a function of pressure. A bridge circuit is used to measure the (reversible) oxidation/reduction rates in selected redox couples. Measurements can be made in a hydrostatic pressure environment to about 100 MPa.

Sato and Nakayama (1974) reported the results of electrolysis studies on the two ion couples ferrocyanide-ferricyanide and ferrocene-ferricinium. Analyses of these data led to an apparent complex behavior of the diffusion constant in these systems. Efforts to resolve some of the questions raised in this work are underway.

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J. KYOTO UNIVERSITY (KU)

1. Introduction

A bill, introduced at the fourth session of the Imperial Diet in 1892, called for the creation of Kyoto University (KU) for the purpose of pursuing academic research and to provide competition for the, even then, formidable University of Tokyo. KU was officially established in 1897 and today continues to provide very high standards of excellence in academic research, not only for the University of Tokyo, but the entire world. This statement is especially true in the field of high pressure science and technology, for it is said that modern high pressure research in Japan had its birth at KU. As early as 1935, Professors Horiva and Kiyama were engaged in the study of chemical reactions under conditions of elevated pressure. Some of the original equipment designed and built by Professor Kiyama, e.g., a lever-dead weight press, constructed over 40 years ago, is still in use today.

With this early start, it is no wonder that KU continues to be a pioneer in high pressure research in Japan. Today there are four independent groups at KU working on scientific problems with a common denominator of high pressure. Perhaps the largest of these groups is that of Professor Jiro Osugi in the Department of Chemistry, where the primary interest continues to be the study of chemical reactions under varying thermodynamic conditions. Two groups are found in the Department of Physics, those of Professors Asai and Endo. Professor Asai and his co-worker are mainly concerned with the high pressure structural properties of various polymers, whereas the high pressure interests of Professor Endo's group are directed toward the investigation of liquids, e.g., alkali metals and Hg. The fourth group is located on the other side of Kyoto at the Abuyama Seismological Observatory, where Professor Mitsuhiko Shimada and his co-worker are pursuing research related toward geophysical and geochemical interests.

2. Division of Physical Chemistry

The Division of Physical Chemistry is contained within the Department of Chemistry in the Faculty of Science and headed by Professor Jiro Osugi. It is a most formidable task indeed to attempt to summarize the output of this group in recent years; in the period from 1972 to 1975 alone, there were more than

30 publications involving high pressure studies. Much of this work is focused on the evaluation and characterization of chemical reactions under conditions of varying pressure and temperature. The fundamental objective is to gain an understanding of the mechanisms of chemical transformation in both solutions and solid-state reactions. A review of this latter area was published by Osugi et al. (1975) and, as a specific example, recent studies by this group of the (Zn, As) system are reviewed here:

The reaction rates of elemental Zn and As to form Zn_3As_2 were studied in the (P,T)-range, of 2 to 4 GPa and 150 to 400 C by Katayama et al. (1975). The reactions were carried out at various (P,T)-conditions in a cubic-anvil press equipped for electrical heating. After specific reaction times, the products were quenched and subsequently analyzed by x-ray diffraction techniques to determine the amounts of Zn_3As_2 and unreacted elements present; thus reaction yield-time curves were determined.

Based on detailed analyses of these data, it was concluded that the initial process in the reaction was phase-boundary controlled and that the kinetics were similar to those of "ordinary chemical reactions." Appropriate values for both the activation volumes and energies were determined. However, because increased pressure tended to retard the reaction rate; it was deduced that the latter stage of the reaction was diffusion controlled; again values for the activation volumes and energies were evaluated. Moreover, by utlization of the Kirkendall effect, i.e., the interposition of an inert marker, in this case Pt, the diffusing specie can be identified. Subsequent electron microprobe analysis definitely identified this as Zn. Studies on other systems have followed from this, e.g., the Zn-Sb (Katayama et al. 1977), Ni-Sb, and Cd-Sb systems.

Other high pressure studies underway in this group involve both electrical conductivity and spectroscopic measurements. A wide variety of high pressure gear is also in use: as a matter of fact Professor Osugi was the recipient of a national award in technology in 1964 for the fabrication and operation of the first Japanese cubic-anvil press. There are now two cubic presses in operation at KU, each provided with high temperature capabilities, and one with a solid-state energy dispersive diffraction system. There are also a large number of other presses available for research: a two-stage press, girdle-apparatus and a number of piston-cylinder systems. Various types of hydraulic apparatus are also used for introducing liquid chemical reactants into a high pressure environment and subsequently sampling the product.

On the whole this group has been, and for many years to come will continue to be, active on the forefronts of high pressure research of chemical reactions.

3. Department of Physics

As noted above, Professor Asai and his co-workers are interested in the high pressure structural properties of polymers. Their work involves x-ray diffraction measurements made in a gasketed diamond-anvil pressure cell up to

about 2.2 GPa. This cell is also equipped with an electrical heater which permits heating of the pressure cavity to about 300 C; the temperature is controlled independently on each diamond anvil and estimated to be stable within 0.5 C.

Results have been reported on the high pressure structure and compressibility of polyoxymethylene (Miyaji and Asai, 1974; Miyaji, 1975) and, most recently, on the similar properties of polyethylene (Yamamoto et al., 1976 and 1977).

The high pressure activities of Professor Endo's group are focused on the electrical and structural properties of liquid metals. The structural studies (pursued in collaboration with Professor Minomura of the University of Tokyo) are performed in a Be-bomb hydraulically pressurized up to about 400 MPa. Application of an electrical heater permits simultaneous elevated temperature studies up to about 140 C. Standard x-ray diffraction methods are used to record the scattered intensity profile up to ± 37 in 2θ. Contributions to the measured intensity from the Be container are deleted and other standard x-ray corrections applied. The resultant intensity profiles are then analyzed in terms of their pressure dependence. (In the opinion of this author, it would be worthwhile to attempt to take the analysis one step further and actually compute the Fourier transforms of the reduced intensity profiles, thereby revealing the appropriate radial distribution functions). The shifts in the intensity profiles are combined with compressibility data to provide volume dependence of the profile peak position. This information is then analyzed in terms of appropriate hard-sphere models for these liquids. It is found that, in the case of Na, K, and Cs, a fixed packing fraction model is adequate to explain the data (Tsuji et al., 1975). Studies presently underway in this laboratory include the high pressure properties of liquid-Te which, apparently, has a semiconductor-to-metal transition in the liquid state.

Using a similar facility, this same group has also undertaken the study of electrical properties as a function of pressure. The pressure dependence of electric transport properties, e.g., electrical resistivity and thermoelectric power of Cs, Rb, K, Cs-Na alloys, and Cs-K alloys have been studied up to 3 GPa (Oshima et al., 1974). In all cases, a rather strong effect is seen and, in the case of Cs, a maximum in the thermoelectric power is exhibited at about 1.6 GPa, which is interpreted in terms of pressure induced changes in the Fermi energy levels and the d-band electronic states. More recently Tsuji et al. (1977) have carried out similar measurements in Hg and Hg-Cd amalgams. Work on this program is still underway.

4. Abuyama Seismological Observatory (ASO)

The high pressure research underway at the Abuyama Seismological Observatory (ASO) is considerable. Built in 1930, this laboratory now serves as the data processing center for seismic information relayed from data stations located over the entire northern part of the Kinki District. In addition to investigations regarding the seismology of earthquakes, this laboratory is also involved in static high pressure research on materials of geological interest. The fundamental objectives of this work are to learn more of the physical and geochemical details of the earth's interior.

A variety of high pressure gear is currently being used for research at ASO; 400 and 500 ton hydraulic presses are used in a girdle arrangement with several different girdle sizes providing upper pressure limits of 3, 5, and 8 GPa. Professor Shimada (1974) has paid particular attention to the reproducibility, high temperature pressure calibration (to 1100 C), and effects of repeated pressure cycling in this belted apparatus. There is also a smaller press used for uniaxial compression studies and fracturing rocks; its upper pressure limit is about 500 MPa. The heart of the high pressure apparatus at ASO, however, is a cubic press; it has six-independently controlled hydraulic rams each rated at 500 tons. This press was installed in 1973 and built by Riken-Koki Company. Although routinely operated to pressures of about 6 GPa, in a cubic volume 2 cm on an edge, it was estimated that, using their smaller 1 cm cube, pressures approaching 12 GPa could be realized; photographs of the press are shown in Fig. II-J-1. Most data obtained from this system are either from quenched samples or pressure dependent electrical resistivity data.

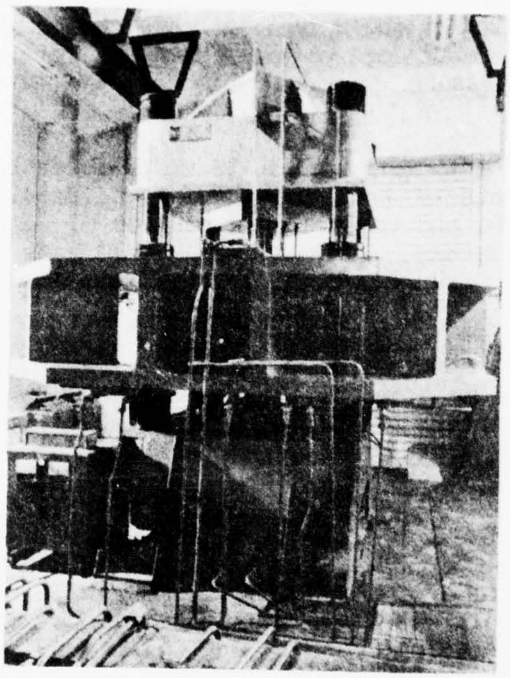
A single stage piston-cylinder apparatus with a 12 mm diameter bore is equipped for simultaneous measurements of both the thermal diffusivity and conductivity at pressures up to 4 GPa and temperatures to 1000 C. Based on careful calibration studies in this system, against known transitions in Bi, KCl, and quartz-coesite, Professor Shimada estimates the precision in pressure determination to be within $\pm$0.05 GPa.

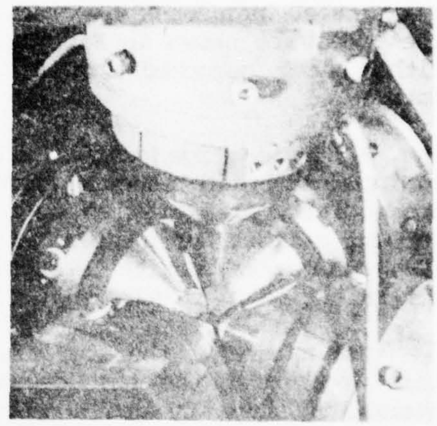
The nature of the high pressure experimental measurements carried out by this group over the last decade can be grouped into three categories: (1) *thermal diffusivity and conductivity*, (2) *electrical conductivity*, and (3) melting parameters. In all cases, as noted above, the studies are related to materials of geological interests.

Yukutake (1974) has investigated the anisotropy of the thermal diffusivity of quartz up to 700 C and 3.3 GPa. From his data the pressure derivatives of the diffusivity were determined in directions normal and parallel to the c-axis. This information is useful in the evaluation of various theories concerning the isotropy of the earth's interior.

In a similar manner, Yukutake and Shimada (1974) measured the pressure and temperature variation of the thermal diffusivity of KCl from ambient conditions up to 4 GPa and 820 K, respectively; this includes the B1-to-B2 phase transition at 1.9 GPa. Based on an observed large decrease in the thermal diffusivity at the transition, Yukutake and Shimada estimate a substantial reduction in the phonon mean-free path and a change in the phonon velocity.

The electrical conductivity studies have been carried out at ASO exclusively by Dr. Hiroshi Watanabe. Recently he has completed studies on basalt to 2.0 GPa and 1500 C (1970), granite to 2.2 GPa and 1500 C (1972), and very precise measurements on KCl in the range spanning the aforementioned phase transition, i.e., up to 2.0 GPa and from 500 to 900 C (1977). In addition, Watanabe (1975) has determined the effects of pressure and temperature on the rate of recrystallization of synthesized albite glass from his electrical conductivity data.





超高圧発生アンビル部（500ton×6）

六方押しプレス

Fig. II-J-1: Photographs of the cubic press in use at the Abuyama Seismological Observatory, Kyoto University. Each of the six rams are independently controlled and have a force limit of 500-tons.

Finally, Shimada (1969 and 1972) has examined the melting properties of albite ($NaAlSi_3O_8$) in the presence of water. This work is important from a geophysical point of view because of the probable presence of water in the earth's crust and the fact that water generally tends to depress the melting point of silicates. This was also found to be the case for albite.

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K. KYUSHU UNIVERSITY (KSU)

1. Introduction

Kyushu University (KSU) is located in the city of Fukuoka on the southern Japanese island of Kyushu. Fukuoka is about 1170 km (730 mi.) from Tokyo and can be reached in about seven hours by train or within one hour by air. KSU was founded in 1911 as Kyushu Imperial University; in 1949, with the reorganization of the Japanese educational system, the school was given the name it bears today.

High pressure work at KSU may be found in the Institute of Applied Science under Professor Tetuo Takemura and in the Department of Applied Chemistry under Professor Motowo Takayanagi. Both groups are studying inter alia, the effects of pressure on various properties of polymers.

2. Institute of Applied Science

The Institute of Applied Science is extremely well equipped for a variety of high pressure experiments; they have operational capabilities for measurements in each of the following areas: x-ray diffraction, DTA, thermal expansivity, NMR, ultrasonic velocities, and tensile properties. They have a diamond-anvil pressure cell and are also set up for laser related measurements, viz., both Raman scattering and ruby fluorescence. Both Ar and He-Ne lasers are being used.

One of the most impressive operations in this group is a high speed x-ray diffraction system. A Be bomb is equipped with heating coils for operation to several hundred C and pressurized to several hundred MPa with low viscosity Si-oil (supplied by Toshiba (TSF-45)). Ni filtered radiation generated in a Cu x-ray tube operated at 55 KV and 70 ma is scattered by the sample in the Be bomb and analyzed with a position sensitive proportional counter (PSPC). This PSPC was developed at Osaka University by Professor Yasusada Yamada and is now commerically available from Rigaku Denki Co. (cf. Part II-S-4b). The PSPC system is extremely rapid: diffraction patterns from a polycrystalline polyvinylidene fluoride (PVDF) could be obtained within seconds. The system is so rapid in fact, that in this study of PVDF, the structural data are recorded at the same rate of heating as the DTA measurement, i.e., 5 C/min. Consequently each of the various transformations indicated on the DTA plot could be confirmed on the accompanying x-ray diffraction patterns (Yasumiwa et al., 1976).

By means of this system, Matsushige et al. (1978) have reported direct observations of the crystal transformation processes in PVDF. Work in this group continues with particular emphasis on the high pressure-high temperature structural and related properties of polymers.

3. Department of Applied Chemistry

The work in this department is very effectively directed by Professor Motowo Takayanagi who was recently recognized for his many noteworthy achieve-

ments in the field of plastics and polymers with the Society of Plastics Engineers Educator Award. Among other things, he is concerned with pressure effects on the basic physical properties of polymers.

A major pressure related activity here is the study of solid-state extrusion techniques of polymers. Using a tapered-die and ram-cylinder system Professor Takayanagi and his co-workers discovered that, at temperatures below the melting temperature, a crystallographic phase change occurs under extrusion from an elastic to a visco-elastic state and, in this latter form, deformation takes place in the absence of thermal distortion, resulting in a high elastic modulus for the extrudates. Takayanagi (1974) has explained the details of this strain hardening behavior in polymers through a theoretical model. These calcualtions give excellent agreement with experiment and allow prediction of ideal extrusion conditions of polymers based on the unfoldability parameter of molecules in lamellar crystals, the strain-hardening parameter, the initial yield stress, and the tenacity of fibers.

Other recent pressure related studies by this group include the following: ultrasonic properties of poly (γ-methyl D-glutamate) film in the α-helical conformation under pressure (Yoshizumi et al., 1977), temperature and pressure dependences of the Grüneisen parameter of polyethylene (Kijima et al., 1975), effect of pressure on the α_2-relaxation of polyethylene single crystals (Kijima et al., 1974), and the effect of pressure on the entropy of fusion of extended chain crystals of polyethylene (Takayanagi et al., 1974).

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L. NAGASAKI INSTITUTE OF TECHNOLOGY (NIT)

Nagasaki Institute of Technology (NIT) is a small, private, co-educational university located on the outskirts of Nagasaki, geographically perhaps the most western major city in Japan. The school was started in 1943 on Koyagi Island, near Nagasaki Harbor, as the Nagasaki Naval Architecture Professional School; it later became known as Nagasaki Junior College of Naval Architecture. In 1958 the campus was moved to its present site in Aba-machi and college status was achieved in 1965 under the new name Nagasaki Institute of Technology (Nagasaki Zosen Daigaku). In 1976 graduate programs in hydraulic and structural engineering were added to the curriculum.

There are only very limited high pressure studies underway at NIT and these are located in the Department of Chemistry under the direction of Professor Masao Tsuchiya.

High pressure activities are just now getting underway. Basically the program is focused on structural and molecular interactions in aqueous solutions. Using a variable temperature pressure bomb similar to that employed in Professor Keizo Suzuki's laboratory at Ritsumeikan University (cf. Part II-U), the solidification points of various solutions are measured optically. The point of transformation is identified by a cloudy, milky appearance in the solution and the P, T coordinates are very accurately noted. Work is scheduled to get underway to investigate the solubility of the following polyethylene glycol compounds: mono-p-nonylphenyl ether, mono-n-dodecyl ether, monooleyl ether, and glycerol monostearate.

M. NAGOYA UNIVERSITY (NU)

1. Introduction

The history of Nagoya University (NU), which is said to be the smallest of the Japanese "Big 7 Universities," dates back to 1871. The School of Science and Engineering, however, was founded comparatively recently in 1939; in 1942 it was subdivided into the School of Science and the School of Engineering. Today research in high pressure is underway in three different groups at NU: the Department of Earth Sciences, the Department of Mechanical Engineering, and the Synthetic Crystal Research Laboratory.

2. Department of Earth Sciences

a. Multiple-Anvil Sliding System (MASS)

One of the more impressive high pressure facilities in Japan is the mammoth 10^4-ton press currently under construction under the supervision of Professor Mineo Kumazawa in the Department of Earth Sciences. Perhaps one of the most innovative ideas in the area of high pressure research in recent years is the concept of the multiple-anvil-sliding-system or MASS as it is more commonly known. Although there are earlier references to the MASS concept in the literature, cf. Hall (1960) and Epain et al. (1967), the idea

was independently conceived and developed in depth by Professor Kumazawa and his co-workers at NU (Kumazawa, 1971 and 1973; Kumazawa et al., 1972 and 1975).

The complete details of the MASS concept are somewhat involved, but briefly MASS involves a motion, in concert, of multiple components of a pressure container, generally activated by a uniaxial compressive force. Necessary lateral forces are generated by appropriate directional components in response to the particular type of MASS-geometry employed. The MASS concept is represented schematically in Fig. II-M-1 and one of the simpler cubic-configurations (called MASS 318-90 by Kumazawa (1977)) is shown in Fig. II-M-2. Many different and complex geometries are possible and, in the aforementioned references, many have been analyzed in detail by Kumazawa. The general advantage of this system over the more commonly used piston-cylinder, supported anvil (belt or girdle design), or multiple anvil facilities, is that the geometry can be designed to take the greatest advantage of the support strength of the anvil materials, hence usually leading to greater pressures in a comparatively large volume chamber.

As noted above, much, if not all, of the developmental work on MASS has been carried out at NU. At present there is a MASS in operation in the NU 10^3-ton press: pressures are measured in this system by the usual calibration of the applied load against known pressure induced electrical transitions. Based on a non-linear extrapolation above the GaP-transition at 22 GPa, Professor Kumazawa (1977) estimates that pressures in excess of 50 GPa have been reached in a cavity of 20 mm^3 volume.

While this 50 GPa facility continues to be used for both scientific and MASS apparatus development, the aforementioned 10^4-ton press and its associated hardware are rapidly nearing completion. Housed in a separate building especially constructed for this facility, the new system is designed to be virtually all automatic. The motion of the various parts can be controlled entirely from either of two electrical control panels by a single operator. As it was explained, for purposes of reducing construction costs, fabrication of the facility was contracted to the Boliter Company, a small machining company in the Nagoya area; they, in turn, subcontracted most of the work to the large Mitsubishi organization. Professor Kumazawa did not care to estimate the ultimate pressure producing capabilities of his 10^4-ton MASS facility, he simply smiled knowingly at my suggestion of "1+ megabars."

Much of the apparatus is currently working and the entire system will probably be fully operational within the next year. A new sample and gasket preparation room and an x-ray diffractometer for on-site examination of quenched products are also located in this new building.

b. Energy Dispersive X-Ray Measurements

Perhaps one of the greatest disadvantages of the MASS facility, like that of many other large, hydraulic systems, is the difficulty involved in extracting useful data. By and large, the most common type of in situ measurement is electrical resistance and for this reason known pressure dependent electrical transitions are frequently used to calibrate load curves. In an

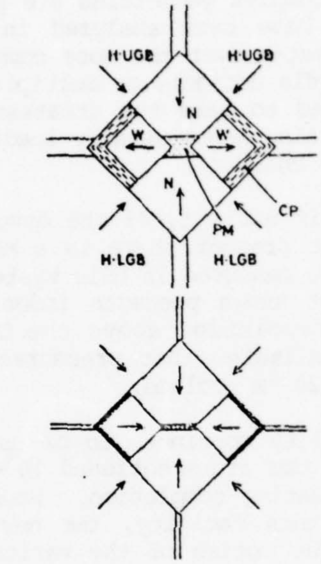

Fig. II-M-1: Schematic of the operation of the MASS mechanism. In the upper drawing the heads of the upper and lower guide blocks (H-UGB and H-LGB) are displaced in the direction of the arrows during pressurization; the resulting motion of the normal (N) and wedge (W) anvils are also indicated by arrows. In the lower drawing the force directions in the pressurized state are shown by the arrows; the compressible pads (CP) and the pressure medium (PM) are shown in their compressed state (from Kumazawa, 1977).

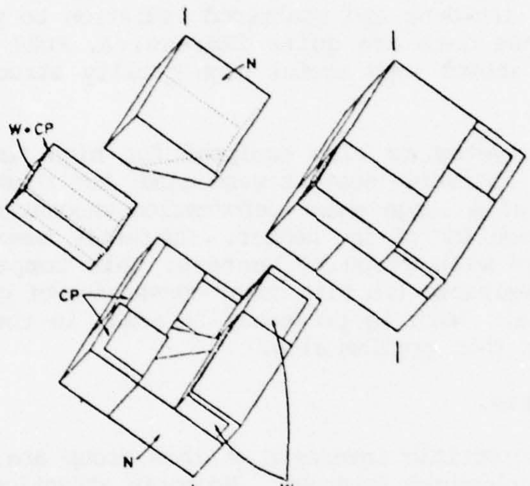

Fig. II-M-2: Geometry of MASS 318-90 type anvil assembly. On the left, a normal anvil (N), wedge anvil (W) combined with two compressible pads (CP), and pressure medium are removed from the cube-shaped assembly. On the right, the pressure medium is set between the two truncated faces of the normal anvils.

effort to also obtain in situ structural data, work is underway in the 10^3-ton press facility to carry out high pressure x-ray MASS measurements.

An extremely intense polychromatic incident x-ray beam is produced with a rotating Au target; the tube can be operated at a power of 8 kw (50 kV; 160 ma), substantially above the 750 w (50 kV; 15 ma) of, for example, a conventional Mo x-ray tube. Very well defined NaCl energy dispersive diffraction patterns were obtained from this system using an intrinsic Ge solid state detector having a resolution of 500 eV at 400 keV (Canberra Insustries). The pattern was recorded at a diffraction angle (2θ) of 16^o in a period of 1500 sec; the following NaCl diffraction peaks were easily discernible: (111), (200), (220), (222), (420), and (440). Considering that it is necessary for both the incident and scattered radiation to pass through a boron-epoxy gasket, these data are quite impressive. Full utilization of this capability should afford much useful high quality structural data at ultra-high pressures.

The existing system is also equipped for high temperature operations. Initially metallic resistive heaters were used, but these proved to be unsatisfactory because of a large shear deformation encountered at elevated loads and resulting degradation of the heater. Currently temperatures up to 1500 C are being achieved with graphite heaters; this temperature limit is due largely to the undesirable (in this case) conversion of graphite to diamond at higher temperatures. Work is presently underway in the Department of Earth Sciences to address this problem also.

c. Research Program

The general scientific interests of this group are, of course, directed to materials of geophysical interest. Recently attention has been focused on various Mg and Fe compounds. For example, x-ray studies of quenched samples of spinel-$MgAl_2O_4$ have revealed that the decomposition into an oxide mixture of MgO and Al_2O_3 occurs in the 20 to 30 GPa range; this observation is in conflict with previous thermodynamic calculations predicting decomposition at 15.3 GPa. The source of this discrepancy is believed to be due to inaccurate thermodynamic data (Ohtani et al., 1974).

Other studies have been carried out on Mg_2SiO_4 (Kumazawa et al., 1974), Fe_2SiO_4 (Sawamoto et al., 1974), and (Mg, Fe)SiO_3 (Sawamoto, 1977).

3. Department of Mechanical Engineering

High pressure studies in the Department of Mechanical Engineering are presently focused on the phase diagrams of the Al-Si and Cu-Zn systems. Interests in these materials are related to the fact that they are frequently used as casting materials. In particular, Mii et al. (1976) have examined the effect of pressure on the solubility of Si in Al. A significant effect was observed, i.e., the 1.59 at. % limit at ambient pressures was increased to more than 15 at. % at 5.4 GPa resulting in a much harder quenched alloy.

The high pressure research in this Department is generally pursued in

one of several cubic-anvil presses; compression in a 1200-ton press of a 15 mm edge length cube yields static pressures up to 8 GPa. Temperatures up to 1000 C are obtained in the pressure chamber by carbon resistive heating. As with most apparatus of this type, the pressure is estimated by prior calibration of the load against various known calibrants, e.g., those used here are the Bi I-II (2.54 GPa), the Tl II-III (3.67 GPa), and the Ba I-II (5.5 GPa).

A separate cubic press with 6 mm faces is capable of producing pressures up to 9 GPa and has been equipped with a rotating anode x-ray tube and an associated diffractometer. The vertical position of the entire diffraction apparatus can be micro-adjusted through 20 mm to accomodate small changes in the position of the pressure cavity with varying load. The scattered radiation is recorded with a NaI(Tl) scintillation detector which can span an angular range of $\pm 35^{\circ}$ in 2Θ; moreover, the reading of the angular position is estimated to be accurate to within $\pm 0.004^{\circ}$. Utilization of this apparatus, plus correction for small changes in the x-ray scattering center during a pressure run, yields high pressure lattice parameters to an accuracy within $\pm 0.02\%$ — a very impressive achievement.

Initial application of this facility has been focused on precise measurements of the compressibilities of Al, Si, and Al-Si alloys (Senoo et al., 1976a and b). Furthermore, in an effort to obtain truly hydrostatic high pressure conditions, the samples used in this system are frequently encapsulated in a 4:1::methanol:ethanol solution. The results of the compressibility studies on Si were found to be in conflict with previous data obtained from solid pressure media, and hence non-hydrostatic pressures.

Other related studies of this group have been concerned with assessment of the pressure-corrections for thermocouple emfs (Fujishiro et al., 1974), psuedo-potential calculations of the compressibility of several cubic metals (Seno et al., 1976), and examination of the tensile behavior of polycrystalline Zn samples at pressures up to 200 MPa (Nakajima et al., 1977).

4. Synthetic Crystal Research Laboratory

One application of elevated pressures in this Laboratory has been for the production of single crystals which, because of thermodynamic contraints, cannot be produced under ambient conditions using normal melt-growth techniques. As an example, single crystals of CsCl were produced in the B2-structure from the liquid phase by raising the pressure in the growth chamber above the triple point pressure at about 97 MPa (Midorikawa et al., 1974).

The pressure interests of this group are actually much more extensive than this: considerable work has been carried out on pressure induced transitions in various dielectrics. Two recent studies include measurements of the spontaneous polarizations and dielectric parameters of KNO_3 under hydrostatic pressures up to about 3 GPa (Midorikawa et al., 1971) and measurements of selected phase transitions in $CsSrCl_3$ up to about 300 MPa (Midorikawa et al., 1976). In both cases, the experimental observations were followed up by copious theoretical evaluations.

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N. NATIONAL INDUSTRIAL RESEARCH INSTITUTE OF KYUSHU (NIRIK)

1. Introduction

The National Industrial Research Institute of Kyushu (NIRIK) is located in the city of Tosu about 25 km (or 15 miles) south of Fukuoka on the southern island of Kyushu. The Institute was established in 1964 to "...promote the technological advancement in machinery, metal, and chemical industry...." Today NIRIK is involved in programs on the development of new materials including polymeric compounds, new composites, and inorganic structural materials. R&D on measurement techniques, especially mechanical testing, is also actively pursued.

The pressure related work at NIRIK is mainly related to materials preparation, e.g., hot pressing and sintering, in particular on carbon compacts and TiB_2 compounds, respectively.

2. Sintered Polycrystalline Carbon

Work is now in progress on various carbon materials to study the effect of the reaction conditions on the resulting compact. Specifically, the effect of adding B_2O_3 as an aqueous solution to various types of carbon powders, e.g., pitch coke, petroleum coke, and pyrolytic carbon, to mention a few, was studied. After drying, the mixtures were hot pressed at varying temperatures up to 2200 C and at about 20 MPa pressure.

Some of the conclusions arrived at are: (1) if pressures in excess of 20 MPa were used, the reaction temperature could be lowered without degradation of the properties of the compacts; in the case of pitch coke, (2) pressing temperatures above 2000 C are required to obtain dense and strong polycrystalline graphite and (3) the addition of boron carbide has the effect of accelerating the graphitization of coke.

In a very recent discovery, only indirectly related to high pressure, Kobayashi et al. (1978) found that dense, high strength carbon composites could be formed without the need of a pitch binder. The process calls for initially grinding green petroleum coke for varying lengths of time followed by compaction at about 200 MPa and then heat treated to 2700 C in an ambient pressure Ar environment. Many of the measured physical and mechanical properties—bulk density, porosity, hardness and compressive strength were found to improve with increased grinding time of the green petroleum coke. Investigations are currently underway to characterize the nature and extent of the changes produced in the grinding process.

3. Sintering Studies

Work is also underway on sintering of TiB_2 powder and TiB_2-Ni mixed powder. A girdle-type apparatus is used for this work with the sample contained in a graphite cylinder for heating purposes. Temperatures approaching 2500 C can be attained by passage of an electrical current through the anvils; pressure limits are on the order of several GPa and calibrated against known Bi and Tl transitions.

Watanabe and Kobayashi (1974) reported that the lattice strain produced at very high pressure, as measured from x-ray line broadening, has a close relation to the initial stage of the sintering process, i.e., the process has been viewed as a two-stage operation and, during the first 30 sec (initial stage), there is a very rapid decrease in the number of pores with a concurrent increase in the hardness.

More recently, Watanabe (1977) has shown that powders of TiB_2 + 20% Ni and TiB_2 could be sintered to more dense forms with and without, respectively, a chemical reaction within 20 sec. Again, the internal lattice strain is believed to play an important role.

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O. NATIONAL INSTITUTE FOR RESEARCHERS IN INORGANIC MATERIALS (NIRIM):

1. Introduction

The National Institute for Researchers in Inorganic Materials (NIRIM) is located in the "New City of Research and Education" of Tsukuba, near Ibaraki and accessible from Tokyo after a one-hour train ride from Ueno Station. NIRIM was created in April, 1966, as an independent, national research institute following extensive discussions which began in July, 1963, concerning the need for basic research in science and technology. It was felt that strong demands existed in Japan and the world for inorganic compound materials with new or unique properties. NIRIM was created for the purpose of fulfilling these demands. The Institute bases its research upon an interrelation between the following three areas: syntheses studies, analyses of chemical compounds and structures, and characterization of properties.

2. High Pressure Research

a. Programs Employing High Pressure Techniques

There are fifteen research groups at NIRIM each representing eight or nine people and having an estimated lifetime of about five years; four of these groups are involved in pressure related programs: the 4th Research Group, headed by Dr. Kenji Uchida, is conducting research on aluminum oxide (Al_2O_3); the 5th Research Group, headed by Dr. Bin Okai, is involved in studies of phase transitions in perovskite-type compounds; the 6th Research

Group, headed by Dr. Minoru Iwata, is conducting research on boron nitride; the 8th Research Group, headed by Dr. Nobuo Setaka, conducts similar studies on diamond synthesis. In addition, there is a section consisting of four people headed by Dr. Osamu Fukunaga devoted to the operation and maintenance of the high pressure research facilities.

As summarized in the 1977 edition of the NIRIM brochure, the objectives of each of these groups are as follows:

"FOURTH RESEARCH GROUP (Aluminum Oxide: Al_2O_3)

Objectives of research

Synthesis, chemical and electromagnetic properties, analysis of defect structures and growth of single crystals of aluminum oxide are studied in order to find practical applications as catalyst, solid state electronic material, abrasive and solar energy absorbent.

Research program

1. Synthesis
   (a) Preparation of aluminum oxide by anodic oxidation of aluminum plate in sulfuric-oxalic acid bath.
   (b) Synthesis of the suboxides of aluminum.
   (c) Synthesis of x-Al_2O_3 from q-Al_2O_3 under the action of high pressures.
2. Chemical properties of aluminum oxides.
3. Solid state reaction of aluminum oxide with cobalt oxide.
4. Electromagnetic properties of alumina materials containing transition elements.
5. Alumina as abrasive.
6. Crystal growth and dielectric structure of corundum.
7. Alumilite as solar energy absorbent.

FIFTH RESEARCH GROUP (Perovskite-type Compounds: $Pb_{1-x}TiO_{3-x}$)

Objectives of research

For use of perovskite-type compounds as electronic materials, synthesis and property analysis under ordinary and high pressures are carried out together with examination of disordered structures, non-equilibrium defects and structural changes.

Research program

1. Synthesis
   (a) Synthesis of defective perovskite-type compounds.
   (b) Amorphous states and their crystallization.
2. Properties
   (a) Properties of defective perovskite-type compounds.
   (b) Electronic and magnetic properties of perovskite-type compounds.
   (c) Phase transition in group IV elements and III-V compounds at high pressures.
3. Generation of very high pressures and high pressure synthesis.

SIXTH RESEARCH GROUP (Boron Nitride: BN)

Objectives of research

To find applications of boron nitride (BN) as refractories and super-hard and electronic materials, studies are made on the preparation of the high purity materials, growth of single crystals, sintering and synthesis under high pressures. The structures and physical properties are also investigated.

Research program

1. Synthesis and growth of single crystals of BN by the flux method, the sublimation method, etc.
2. Synthesis and sintering of boron nitride under high pressure.
   (a) Stability relationship among polymorphs.
   (b) Catalysts for synthesis of cubic BN.
   (c) Development of the apparatus for synthesis under high pressure.
   (d) Sintering of cubic BN powders.
   (e) Surface structures of cubic BN crystals.
3. Preparation and properties of the thin films.
4. Measurements of optical properties.

EIGHTH RESEARCH GROUP (Diamond: C)

Objectives of Research

For use of diamond as super-hard and electronic materials, studies are made on the growth of high purity single crystals and the preparation of thin films. Major efforts are made on elucidation of the processes of growth and transformation from the viewpoint of surface chemistry and crystallography.

Research program

Synthesis of diamond under high pressures.

(a) Development of high pressure cell.

(b) Growth of high quality single crystals by the molten metal solvent catalyst method.

(c) Crystal structure and transformation.

2. Surface chemistry of diamond.
3. Preparation of diamond thin film.

(a) Synthesis of film by the chemical vapor deposition method.

(b) Synthesis of the film by the molecular beam method.

HIGH-PRESSURE RESEARCH STATION

Research program

1. Development of the techniques for a scaled up reaction space in a high pressure apparatus.
2. Generation of very high pressures.
3. Measurements of pressure value in a very high pressure region and establishment of the measuring systems."

b. High Pressure Equipment

The main high pressure facilities at NIRIM are housed in a multi-floor building that was begun in 1968 and completed in October 1971. Although the laboratories are bare of "frills," they do appear to be quite functional and active. Like many high pressure research groups today, the work at NIRIM can be divided into two areas on the basis of equipment: that performed in the large, hydraulically operated gear and that associated with the compact diamond-anvil pressure cells.

The diamond cell work at the Institute is actually very recent, a major effort in this area was started in the fall of 1977 by Dr. Okai's 5th Research Group. The diamond cell being used at NIRIM is the "Ken-ichi" cell designed by Professor Minomura of the University of Tokyo (cf. Part II-Z-2a). Current support efforts include assemblage of a laser and associated spectroscopic equipment for ruby fluorescence pressure measurements, introduction of fiber optics for convenient handling of the optical signals, utilization of a CW YAG-laser for purposes of heating the pressure cavity, and initiation of x-ray studies involving both energy dispersive, solid state detectors, e.g., Si(Li), and photoemission spectra capabilities. The x-ray measurements will be supported by a Rigaku rotating anode x-ray generator with very high power capabilities, viz., 0.2 amp at 60 kV.

The massive hydraulic apparatus forms the backbone of the current high pressure research facilities at NIRIM. Although much of this equipment is perhaps more than ten years old, it continues to render consistent and reli-

able high pressure service. There are four belt-type presses with upper pressure limits in the 3 to 6 GPa range. The largest of these is a 14,000 ton press built to NIRIM specifications by the Swedish firm ASEA (Allwanna Svensks Elektriska Artiebolaget) at a cost of about eighty million yen. An Itskevich-type clamp with a BeCu bomb is used for ultrasonic measurements up to 0.8 GPa; it can also be operated down to LN_2 temperatures. A conventional piston-cylinder apparatus equipped with heating capabilities is available for pressures in the 0.5 to 2 GPa range; pressures up to 15 GPa and temperatures up to 900 C can be obtained in a Bridgman anvil press, while a cubic-anvil apparatus is used for some of the diamond synthesis studies as discussed below.

c. Recent Achievements

Recent publications from the Institute in the high pressure area may be divided into three categories: (1) phase equilibrium and transformation studies, (2) materials synthesis, and (3) high pressure equipment considerations.

c(1). Phase Transformations

For the purposes of gaining increased understanding of the MnO_2-system, the MnO_2-Mn_2O_3 phase boundary was traced up to 3 GPa and in the temperature interval from 800 to 1200 C based on x-ray data obtained from quenched samples (Fukunaga et al., 1969). Similarly, based on careful x-ray analyses of other quenched samples, a rather definitive study was completed of the Li_2WO_4 and Li_2MoO_4 phase diagrams; three new phases of Li_2WO_4 were identified in the (P, T)-range up to 16 GPa and 800 C, respectively.

Some of the results arising from this work raise interesting questions concerning the high pressure chemistry of crystal structures of geophysical interest. For example, upon comparison of the high pressure structures of the two aforementioned systems, which are isomorphic under ambient conditions, it was concluded that the similar crystal chemical properties exhibited by Mo and W ions at ambient P and T, e.g., ionic radius and electronegativity, are no longer valid at elevated pressures. At high pressures, the Mo-compound transforms into the spinel structure, whereas the W-compound "would not transform to the spinel structure even under ultra high pressure." (Yamaoka et al., 1973).

Another study recently completed at NIRIM involves the pressure dependence of the second-order phase transition temperatures in $SrTiO_3$ and $KMnF_3$ based on low temperature ultrasonic data. In addition to demonstrating that earlier work on these materials was in error, it was shown that a previous application of the Landau theory of second-order phase transitions to this transformation was invalid above 8.5 GPa. Details of the transformation mechanism in the higher pressure range (above 1 GPa) remain unknown (Okai and Yoshimoto, 1975).

In a more recent work, a new high pressure polymorph of $FeTaO_4$ was

discovered and the phase boundary up to 4 GPa and 1400 C charted (Tamura, 1973).

c(2). Materials Synthesis

Recent high pressure synthesis efforts at NIRIM can be divided into two subcategories: formation of perovskite and other structures of various sulphides and oxides and synthesis of super-hard materials. In the first category, the following materials have been synthesized and characterized at NIRIM over the past ten years: $BaSnS_3$, $SrSnS_3$, and $PbSnS_3$ (Yamaoka and Okai, 1970); ten different ternary metal oxides with the perovskite structure (Fujita et al., 1970); $PbZrS_3$ (Yamaoka, 1972); two forms of Nb_2O_5 (Tamura et al., 1974); SrS_2 (Kawada et al., 1976).

Most of the super-hard materials studies are directed toward diamond synthesis, although some effort has been expended to synthesize cubic boron nitride (cBN). In this latter case, the objective is to determine better catalytic agents for high pressure cBN synthesis (Fukunaga et al., 1974).

Work on diamond synthesis is pursued with the objective of more accurately characterizing both the optimum (P, T)-conditions and the best catalyst metals for diamond growth. (Kanda et al., 1976; Yamaoka et al., 1977a,b). One rather interesting study in this area concerns the etching of diamond by water under high pressure, high temperature conditions. It was discovered that the trigons (triangular etch pits) formed on the octahedral faces of synthetic diamond were very similar to those found on natural diamond. It was concluded that, in all likelihood, natural diamonds are also etched under elevated (P, T)-conditions by aqueous materials within the earth, e.g., silicate magma (Kanda et al., 1977).

c(3). Equipment Studies

One major modification of high pressure equipment at NIRIM involved the design and construction of a supported wedge, girdle apparatus. The change was implemented to increase the volume of the reaction chamber and hence the yield for both the cBN and diamond syntheses studies. In this design, the sample chamber produced by the two WC-anvils is supported radially by six high strength steel wedge segments which are contained by two concentric binding rings. At 6 GPa, the volume of the enlarged cavity is 50 cm^3 (Fukunaga, 1974).

Work has also been published at NIRIM on the mechanical properties of Bridgman anvils. Basically the study involved considerations of the relation between the anvil diameter and the mechanical behavior. Anvil diameters of 26 and 78 mm were found to yield essentially equivalent results up to 13 GPa and, in this configuration, it was found that the gasket material, pyrophyllite, flowed plastically up to 8 GPa, beyond which compression occurs (Okai and Yoshimoto, 1973).

3. Summary

In review, the past activities of the groups at NIRIM have been focused mainly in two areas: stability studies on various oxides and sulphides and formation of super-hard materials. The motivations for the research appear to be purely academic and it was clear to this observer that the researchers themselves were intently interested in basic understanding of the thermodynamics and chemistry involved in the various systems and transformations being studied.

Given the high rate of productivity at NIRIM and the fact that one group is today in the process of assembling a diamond-anvil pressure facility with many sophisticated data collection capabilities, some very exciting work may be expected of this laboratory in the next few years.

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P. NATIONAL RESEARCH LABORATORY OF METROLOGY (NRLM)

1. Introduction

The National Research Laboratory of Metrology (NRLM) serves as the national center of standards of measurement and metrological research in Japan. Founded in 1903, the overall objectives of the Laboratory are the establishment and maintenance of scientific and technological standards, development of measurement techniques and apparatus, and the determination of fundamental physical constants. In the area of high pressure measurements and characterization, there is work underway at NRLM in two groups: (1) the Mechanical Metrology Section headed by Dr. Namiteru Hida and (2) the Thermal Measurement Section, under the direction of Dr. Kiyoto Mitsui.

2. Mechanical Metrology Section

High pressure studies in this group are pursued largely by Ken Nishibata. Japanese high pressure standards are established and maintained at NRLM: there are four dead weight piston gauges (DWPG) in operation which set the national pressure standards for Japan, two have pressure limits of 400 MPa and the others are limited to 1.5 and 2.0 GPa. These primary pressure standards, which are similar to the DWPGs used in the United States at the National Bureau of Standards, were manufactured by the Kobe Steel Company. In addition to establishing Japanese pressure standards, these precise instruments are also used to calibrate manganin pressure gauges for both scientific and industrial applications. At a pressure of 1.6 GPa, the uncertainty in the measured pressure is estimated to be less than 0.02%, or 320 kPa. In addition to providing calibration services, these DWPGs have also been used to accurately characterize the freezing point of Hg at 0 C: 756.94 ± 0.20 MPa (Yamamoto, 1975) and, more recently, to provide preliminary values for the two transitions in NH_4F, viz. 0.36 and 1.16 GPa.

Other work in this group involves the development of a manganin resistance manometer (Yamamoto, 1972a and b) and accurate characterization of the ice phase diagram to 900 MPa (Nishibata, 1972). In this latter work, based on dielectric and volume measurements, the L-IV-VI and L-V-VI triple points are reported to be 556.7 MPa; -6.62 C and 634.3 MPa; 0.22 C, respectively.

Other recent studies in this section are centered on the development of a single transducer ultrasonic pressure gauge. Generally two transducers are used to estimate pressure from the variance of the transit time of an ultrasonic pulse in e.g., a quartz specimen. However, by using only a single transducer for both the input and output signals, and suitable time-delay circuitry, the transducer can be kept entirely out of the high pressure chamber, i.e., only the quartz need be in the pressurized region. This apparatus is being developed at NRLM for rapid and accurate pressure measurements up to and above 300 MPa (Nishibata and Okamoto, 1976). A problem being concentrated on at present is the possibility of a phase transition in the quartz sample itself.

3. Thermal Measurement Section

Although the primary concern of this Section is measurement of temperature, the group is also in the process of developing a relatively low pressure gauge for operation at variable temperatures down to that of liquid He. Basically the gauge under development consists of a thin metal diaphram which forms one plate of a parallel-plate capacitor; changes in pressure are detected through variations in the capacitance of the instrument. Designed for operation at pressures up to about 500 MPa, when pressurized to 20% of this limit, the corresponding capacitance change is from 3 to 5.5 pfd. When maintained at a relatively constant temperature, the reproducibility is within 0.1%, however, on thermal cycling, this increases to almost 3% in the worst case. This problem of reproducibility is currently under attack.

4. Summary

Although the number of researchers involved in high pressure studies at NRLM is comparatively small, their work on pressure standardization is important and hopefully future efforts will be directed toward calibration standards in the higher pressure regions, e.g., the 10 to 50 GPa range. Plans are presently underway to move the NRLM facilities to Tsukuba Science City; the new NRLM buildings are expected to be completed in early 1980.

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Q. OKAYAMA UNIVERSITY (OKU)

1. Introduction

Pressure related research at Okayama University (OKU) is pursued at the Institute for Thermal Spring Research (ITSR) located near the Sea of Japan in Tottori Prefecture. The Institute may be reached from Tokyo by air in about one hour or via a night train to Kurayoshi.

The primary mission of ITSR is to study and characterize the geothermal reactions occurring in the hot springs in Japan. In that regard, Sakai and Matsubaya (1977) recently published an in-depth review of the four major categories of thermal water systems in Japan.

There are two faculty members at ITSR involved in high pressure research: Professors Yoshito Matsui and Eiji Ito. Their scientific interests are mainly concerned with problems of a geophysical nature.

2. High Pressure Equipment

Most of the high pressure work done here is carried out in a double-stage split sphere apparatus of the type designed by Professor Kawai and co-workers at Osaka University (cf. Part II-S). The eight inner WC anvils are slightly modified so as to avoid significant reduction in pressure transmission efficiency (Ito et al., in preparation). As described in great detail in Part II-S-2, the eight WC-anvils are surrounded by a spherical rubber gasket and the assembly is immersed in a pressurized oil bath. Maximum pressures of about 200 MPa on the oil, yield 3 to 4 GPa at the first stage, i.e., on the segmented 4 cm cubic anvil; this in turn results in pressures estimated to be in excess of 20 GPa in the second stage volume of about 5 mm^3. The actual pressure in the second stage is calibrated against the oil pressure using several fixed points.

The facility is also equipped with an internal electrical heating system whereby temperatures in excess of 1000 C can be maintained. Generally data are recorded on quenched samples, i.e., after the specimen is held at the prescribed (P,T) conditions for the appropriate time period, it is quenched by removing the electric power to the heater. The pressure is then slowly released and the product recovered for examination under ambient conditions.

3. Research

As noted above, the high pressure interests here are primarily related to problems of geophysical interest. In a very recent study Ito and Matsui (1978) stabilized an orthorhombic $MgSiO_3$ perovskite at about 28 GPa and 1000 C. The unit cell parameters and density were determined from the quenched sample and the conclusion was that this product was closer to the ideal perovskite than the $ScAlO_3$ perovskite.

In another recent study of silicate ilmenites and the post-spinel transformation, Ito and Matsu (1977) conclude that, if the Mg/Fe ratio is high, then there is a "...possibility that ilmenite and related minerals are significant constituents in the lower-half part of the transition zone..."

Several other relatively recent investigations of this group include: "The Absence of Oxide Mixture in High-Pressure Phase of Mg-Silicates" (Ito, 1977), "High-Pressure Decompositions in Cobalt and Nickel Silicates" (Ito, 1976), and "High-Pressure Decompositions in Manganese Silicates and Their Geophysical Implications" (Ito et al., 1974).

4. Summary

Although the size of this group remains comparatively small, the productivity has been maintained at a rather high level in recent years and there is every indication that this situation will continue. There will be a

small period of inactivity in the latter part of 1978 as the high pressure facilities are transferred to a new building at the Institute but after that, investigations of various geophysical systems should resume.

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R. OSAKA CITY UNIVERSITY (OCU)

1. Introduction

Osaka City University (OCU) is a small, municipally operated school which is said to have one of the lowest tuition rates in Japan. It is located in the heart of Osaka, about a twenty-minute train ride from the famed Osaka University.

High pressure work at OCU is carried out by Professor Yoshiaki Ogo and his co-workers in the Department of Applied Chemistry. Basically the pressure related interests of this group are twofold: (1) effect of pressure on the elementary reactions of radical polymerizations and (2) studies of solid-phase reactions of organic compounds under pressure with simultaneous shear deformation--what Professor Ogo refers to as "mechano-chemistry."

2. Effects of Pressure on Radical Polymerization

Very recently Ogo and Yokawa (1977) have summarized more than five years of research on six polymerization systems, viz., styrene (Ogo et al. 1973); methyl methacrylate (Yokawa et al., 1974a); butyl methacrylate (Yokawa et al., 1974b); butyl acrylate (Yokawa et al., 1974c); vinyl acetate (Yokawa et al., 1974d and Yokawa and Ogo, 1976); octyl methacrylate (Yokawa et al., 1977).

These polymerization studies are pursued in a high pressure reactor equipped with fused quartz end windows with optically polished faces. The reactor consists of a 10 cm^3 hypodermic syringe with an optically flat end which is positioned in contact with the quartz window. Pressures up to 100 MPa are transmitted to the samples by means of a hydraulic fluid and measured

with a Bourdon gauge. This apparatus was assembled some time ago at the start of the program and has been performing admirably over the years.

The experimental procedure was to first produce the appropriately prepared monomer, then to polymerize it under conditions of varying pressure and finally analyze the resulting polymer under ambient conditions.

The aforementioned summary concerns the effect of pressure on the propagating and terminating steps of free-radical polymerization. It was found that, regardless of the polymerization type, a linear function could be used to describe the pressure dependence of the logarithmic propagation rate constant. From this it was in turn deduced that the activation volume could be used as a pressure-independent parameter for the propagating step in the sub-100 MPa pressure range. Moreover, by correlating information on the activation volumes and the volume contractions of polymerization, an empirical relation to estimate the pressure dependence of the polymerization step was deduced. Finally, a quadratic polynomial was found to give the best overall representation of the pressure dependence of the logarithmic termination rate constant.

In summary, Ogo and Yokawa (1977) conclude that "...an adequate knowledge of the pressure effect on the individual reactions of polymerization has now been obtained..." however, "...the effect of pressure on the rate of termination still leaves (an) unanswered question." The group at OCU is currently in the process of pursuing the answer to this question.

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S. OSAKA UNIVERSITY (OU)

1. Introduction

Osaka University (OU) houses perhaps the largest collection of independent high pressure research groups in Japan today. Pressure related research is found on the main campus of OU at Toyonaka under the direction of Professor Naoto Kawai in the Department of Material Physics and in the High Pressure Research Laboratory, Professor S. Kume heads up a third group in College of General Eductation, and a fourth group is led by Professor Mitsui Koizumi at the Institute of Scientific and Industrial Research on the Suita Campus of OU.

2. High Pressure Research Laboratory

The High Pressure Research Laboratory headed by Professor Naoto Kawai is contained within the Faculty of Engineering Science of OU and was established for the purpose of providing ultra high pressure, large volume facilities for basic research. At the heart of this laboratory is a multistage split-sphere vessel designed several years ago by Kawai et al. (1973). This facility was completed about five years ago at a cost of about ¥10^8 provided by the Ministry of Education for basic high pressure research. It was estimated that three or four runs are made per day at an operational cost of about $100 per run. A spherical shell of WC (186 mm dia) is segmented into six equal parts. The center of the shell is cut away so as to provide a cubic hole in which are positioned eight WC-cubic anvils. One corner of each of these anvils is truncated thereby forming a central octahedral chamber. Normally either pyrophyllite or MgO is used for the pressure transmitting medium in the octahedral cavity (Kawai et al., 1975a). The dimensions of the various parts are variable depending on the objectives of the experiment. The edge length of the trigonal surface defining the central cavity is varied from 20 to 8.5 mm.

The apparatus is operated in a massive 15,000-ton press, probably the largest in Japan. Four-probe electrical resistance measurements are possible and the pressure is estimated from fixed point calibration curves based on known electrical transitions.

Temperatures up to 2100 C can be achieved in the pressure cavity by electrical heating; the sample temperature is determined from both the electrical power input and from an alumel-chromel thermocouple.

Most recently Nosu et al. (1977a) have obtained pressures up to 7.7 GPa in a volume as large as 43 cm^3 by using sintered magnesia blocks as the pressure transmitting medium. This group feels that the use of magnesia as a pressure transmitting medium may be very important.

Several research programs are presently underway in this facility: Kawai and Endo are measuring the resistivity of manganin to over 20 GPa for purposes of high pressure calibration. Studies are also in progress on the phase diagram of ice to 25 GPa where there are preliminary indications of an order-

disorder transition at reduced temperatures. A preliminary report has already been published by Kawai et al (1975b); this work will be expanded to include neutron scattering measurements, to be carried out in collaboration with a group at Kyoto University.

Work is also in progress on the phase diagram of Ce. To date, three phase transitions have been identified to 20 GPa: these are tentatively identified as γ-to-α, α-to-α', and α'-to-tetragonal. In addition, considerable efforts are being expended in sintered diamond studies as discussed below.

3. Department of Material Physics

a. Apparatus

There is a very effective balance of the high pressure activities in the Department of Material Physics between basic materials research and development of high pressure apparatus. In the latter category considerable attention is given to pressure calibration and in this regard, electrical transistors in various metals and semiconductors are under investigation.

The observed electrical transitions are calibrated against the lattice parameter of NaCl as measured by standard x-ray techniques. It was for this purpose that a new split-cone multi-anvil system was constructed (Ohtani et al., 1977 and Kawai et al., 1975c). The basic idea is similar to that employed in the aforementioned split-sphere apparatus. However in this case provision is made for x-rays to pass between the two conical sections (Fig. II-S-1).

Using this facility in a 2000-ton uniaxial press, the semiconductor-to-metal transitions in several compounds have been measured against NaCl; preliminary results for ZnTe, ZnS, and GaAs are 11.7 ± 0.50, 15.28 ± 0.60, and 18.7 ± 0.6 GPa, respectively. (In the case of ZnS, which is being investigated as part of the NBS round-robin pressure calibration program, it is found that on the down-stroke, the transition occurs at 10.74 ± 0.45 GPa and, moreover, that the transition pressure tends to increase with cycling.) (Ondera, 1978.)

The quality of the x-ray diffraction photographs obtained with this system tends to degrade at elevated pressures (>15 GPa) because of the narrowing gap for the x-ray beam. A program is presently underway to modify the facility in order to correct this problem.

b. Electrical Conductivity Studies and Metallic Hydrogen

Studies of electrical conduction under pressure have long been a major interest of this group. Perhaps one of the most exciting problems in science today is the prospect of metallic hydrogen. Several years ago, Kawai et al. (1975d) reported metallizing hydrogen at elevated pressures and ambient temperature. Since that time, there has been considerable discussion within the international high pressure community concerning this problem. There is a program at OU to attempt to reproduce their results. Motohiro Togaya is

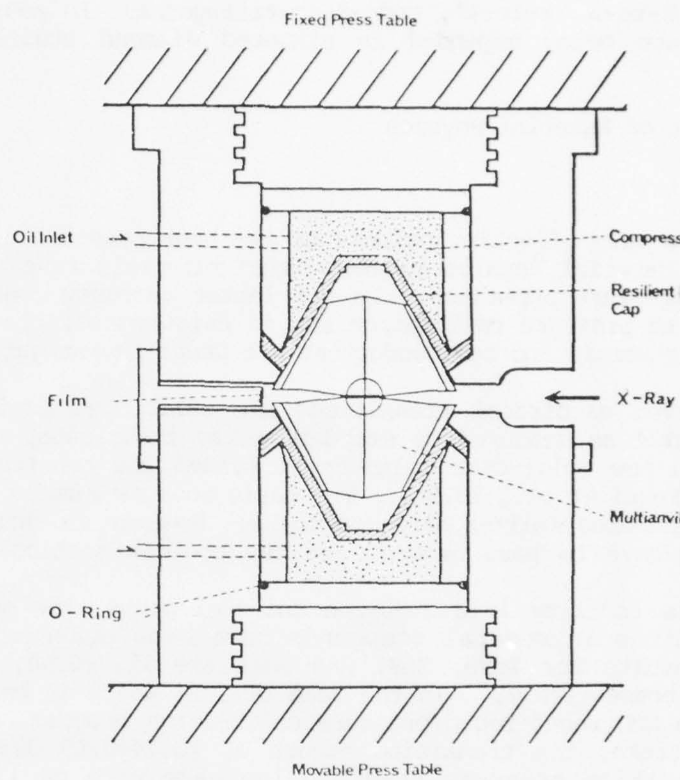

Fig. II-S-1: Split-cone type pressure vessel for x-ray diffractio[n] (from Kawai et al., 1975).

program at OU to attempt to reproduce their results. Motohiro Togaya is presently involved in low temperature pressure calibration, following which he will examine high pressure conductivity in the condensed state of the following gases: CO_2, O_2, Ar, CH_4, NH_3 and H_2.

Electrical conductivity studies carried out recently on other materials at elevated pressures include those on hexaiodobenzene and tetrahalo-p-benzoquinone (Shirotani et al., 1976), one-dimensional metal-glyoximes (Hara et al., 1976), and Si-As-Ti chalcogenide glasses (Hamakawa et al., 1976).

c. Diamond and Other Synthesis Studies

Diamond synthesis research has been underway at OU for several years. A preliminary report on the effects of a Co binder has already been published by Notsu et al. (1975). This March Yukio Notsu completed his doctoral thesis under Professor Kawai; it is entitled, "Sintering of Diamond."

Notsu (1978) used the split-sphere apparatus described above to carry out his investigations. The objective of the work was to sinter a large diamond compact using synthesized diamond powder as a starting material. Actually three different sintering procedures were studied: Case I: direct sintering without a binding material, Case II: indirect sintering using liquid Co, and Case III: indirect sintering using molten Co from WC-Co.

One parameter which Notsu used to compare different compacts was the Knoop microhardness; he cites natural single crystal diamond as having a value of 7 Mg mm^{-2}. (All Knoop hardness values are given in these same dimensions.) By way of comparison, that of commercial compacts ranges from 4 to 6 and natural carbonado is referenced as being no greater than 3.4. The products made by Notsu for Cases II and III cited above, had microhardness values of 7 to 8 (for 7 volume percent of Co binder) and 8.1, respectively. It was further found that, as the reaction temperature was increased from 1400 to 1600 to 1800 C at 8-9 GPa, the microhardness increased from 2 to 5.4 to 7.3, respectively.

Notsu has reached the following three conclusions about his work: (1) pressures and temperatures in excess of 10 GPa and 2000 C, respectively, are required to obtain a single phase diamond compact without a binder; (2) molten Co is helpful in sintering the diamond; and (3) each crystal within the compact has been work-hardened through plastic deformation resulting in a hardness significantly greater than that of natural diamond. It is further argued that one of the major weaknesses of the natural stone, i.e., cleavage, is very effectively removed in the compact thereby resulting in a superior product in the compact.

Considerations are now being given in this area of using the diamond compacts as opposed or multi-anvils for production of higher ultimate pressures. Another synthesis investigation pursued here concerns formation of orthorhombic SnO_2 at 15.8 GPa and 800 C by Suito et al. (1975). Continued studies in this area will be directed toward the similar compounds GeO_2, SiO_2, and PbO_2.

4. College of General Education

a. Mineralogical Studies

Much of the high pressure work of Professor S. Kume and his co-workers in the College of General Education at OU is carried out in collaboration with scientists at the Institute of Scientific and Industrial Research of OU (see below). Basically the interests here are related to materials of geophysical importance.

Simply put, this group is involved in mineralogical studies on quenched samples. A cubic press of the type developed at Kobe Steel, Ltd., (cf., Part II-G-2) is equipped with an internal graphite heater for elevated pressure, temperature studies to 10 GPa and 2300 C, respectively.

One innovation being used here to increase the ultimate pressure in the cubical cavity is to place hardened steel intensifiers on each of the six faces of the pyrophyllite gasket before pressurization. It is estimated that this increased the upper pressure limit by about 20%.

X-ray diffraction analyses on quenched samples constitute the backbone of the research program. Although recently specific heat and magnetic susceptibility measurements on synthesized samples have also been brought to bear on specific problems.

Some of the more recently completed investigations of this group include: synthesis of $EuLn_2S_4$ and $SrLn_2S_4$ (Ln = Lu, Yb, Er, and Y) with the Tl_3P_4-type structure (Ishida et al., 1978), crystal structure of phases produced by disproportionation of K-feldspar under pressure (Kinomura et al., 1977), and transition of sulfospinel to Tl_3P_4-type phase under pressure (Hirota et al., 1976).

b. Position Sensitive Proportional Counter (PSPC)

Although it is not specifically related to high pressure research, the position sensitive proportional counter (PSPC) developed by Professor Yasusada Yamada in this College deserves special mention here. Professor Yamada and his co-workers have been involved for some time in very sensitive x-ray and neutron scattering measurements of materials exhibiting commensurate and incommensurate Jahn-Teller transitions (cf. Noda et al., 1976 and 1977). In order to measure the very weak satellite reflections produced by these structural distortions, Professor Yamada developed a PSPC.

Basically the instrument consists of a cylindrical chamber with a central highly resistive wire and through which a low pressure gas flows. The cylinder is equipped with a thin Be window along one side so as to pass x-ray photons. On entering the cavity the photon gives up its energy by partially ionizing the gas, which in turn results in a voltage pulse at either end of the cylindrical chamber. The relative difference in the two pulse heights provides information about the position of the incident photon. The data are stored in a multichannel analyzer and the number of counts in each channel is,

of course, proportional to the x-ray intensity at that position. Thus, a single measurement gives both position and intensity data. Yamada has used Ar-CH_4 gas for measurements with CuKα radiation and, in collaboration with Professor Minomura of the University of Tokyo (cf. Part II-Z-2a), a 9:1:: krypton: methane mixture for MoKα-radiation; in both cases, the incident radiation was first filtered through a graphite monochromator.

This apparatus seems ideal for weak x-ray scattering experiments--such as those often encountered in high pressure measurements. The system being used by Yamada is 5 cm long and has a position resolution of about 400 μ ; in the configuration in which it is presently being used, the angular breadth in 2θ is 10° and the resolution is about 0.4% or 0.04°. One difficulty of course is that there is a problem in analyzing voltage pulses for high counting rates due to the coincidence problem. Roughly, the maximum incident intensity which the system can handle is about 6000 counts per second.

Rigaku Company has recently announced sales information for such a PSPC x-ray detection system. Additional information about this device is contained in Part II-Z-2a.

5. Research Center of High Pressure Synthesis

The Research Center of High Pressure Synthesis is headed by Professor Mitsue Koizumi and attached to the Institute of Scientific and Industrial Research (ISIR) on the Suita Campus of OU, in the northern suburbs of Osaka. The ISIR, or Sangyo Kagaku Kenkyusho in Japanese, was founded in 1939 as a research institution attached to OU with the objective of fostering the needs of traditional basic and applied science. There are twenty-one research divisions, each representing four to five full-time scientists contained within the following departments: electronics, metallurgy/inorganic chemistry, organic chemistry/biochemistry, and radiation science. In addition, there are several special laboratories at ISIR among which is the Research Center of High Pressure Synthesis.

This Research Center was attached to the ISIR in 1975. Their mission at present is to synthesize inorganic materials, inorganic-organic, and inorganic metal complexes under high pressure, high temperature conditions and to characterize the products.

High pressure apparatus in use here includes a cubic-anvil press equipped with electrical heating capabilities; its operational limits are 10 GPa and 2000 C. A belted piston-cylinder and several hydrothermal units are used for some of the lower pressure studies.

Systems employing different pressure media and their respective limits include: water, 400 MPa; reactive gas (O_2), 200 MPa; inert gas, 300 MPa.

Work is underway today on a broad spectrum of materials, including: attempts to quench $A_2B_8O_{16}$-compounds, e.g., $K_2Al_2Si_6O_{16}$, $K_2Cr_8O_{16}$, or $K_2Mo_8O_{16}$; hot isostatic pressing to sinter BeO, Al_2O_3, and PZT; crystallization of

GeTe and Ge (S, Se, Te)$_2$. Generally these projects are initiated in response to needs from scientists at OU and elsewhere. Often the materials preparation and subsequent analyses are pursued jointly between the team at ISIR and the "outside" scientists.

Several investigations recently completed include the following: "Electrical Behavior of $BaM^{4+}O_3$ (M^{4+}: Mn, Co, Ni) under Very High Pressures" (Shimada et al., 1976), "Transition of Sulfospinel to Th_3P_4-Type Phase under Pressure" (Hirota et al., 1976), and "Synthesis of $K_2SiSi_3O_9$ with Silicon in the 4- and 6-Coordination" (Kinomura et al., 1975).

6. Summary

If a circle with a 30-mile radius were drawn centered on Osaka, both Kyoto and Kobe would fall inside. It is no coincidence therefore that OU represents a bastion on the forefront of high pressure research. There are many groups here using pressure as both a tool, as in many of the material synthesis programs, and as a thermodynamic variable in the investigation of other physical or chemical properties. Virtually all groups visited here appeared to be in a very healthy state and every indication was given that this highly productive environment would continue to flourish.

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T. RESEARCH INSTITUTE FOR POLYMERS AND TEXTILES (RIPT)

1. Introduction

The Research Institute for Polymers and Textiles (RIPT) is a national laboratory supported by the Ministry of International Trade and Industry through the Agency of Industrial Science and Technology. The Institute was founded in 1918 as the Silk Labortory and since that time RIPT has played a leading roll in the development of the polymer and textile industries. The RIPT facilities are presently located in Yokohama and accessible from Tokyo within about 30 minutes by train. In 1979 however, the Institute is scheduled to move to new facilities located in Tsukuba Science City (cf. Part II-O-1).

The research activities at RIPT are contained within five divisions: Bionics, General Research, Polymer Chemistry, Polymer Physics, and Soft Engineering. Pressure related research is concerned with crystallization of polymers under high pressures and hydrostatic extrusion; activities are underway in both the Polymer Chemistry and Physics groups; the groups are headed by Drs. M. Hasegawa and T. Shirota, respectively.

2. Polymer Chemistry

Dr. Yoshio Tanaka and his co-workers are involved in an extremely active program to investigate the effects of pressure on polymerization and thermal decomposition. At the heart of the high pressure equipment being used here is a cubic press similar to the one used by Inoue at Kobe Steel, Ltd., (cf. Part II-G-2). The apparatus was made six years ago by Ishikawa-jima at a cost of ¥16x10^6 and designed by Dr. Wakatuski of Toshiba Electric Company, Ltd. The cubic anvil apparatus is operated in a 500-ton uniaxial press; the maximum

pressure on a 13 mm cube face (reduced to 10 mm in compression) is about 8 GPa. The press can be operated to 400 - 500 C.

This laboratory is also equipped with a rotating Bridgman anvil apparatus for studies of the effect of large shear stresses on solid-solid chemical reactions. For studying charge transfer complexes under pressure, a spectrometer capable of pressures up to 1 GPa and operative in the 210 to 2500 mm range is available. Finally, a 1.5 GPa hydraulic press is used for high pressure polymerization studies.

The nature of the research underway here is actually reflected in the titles of several recent publications: "Radical Polymerizability of N-(4-anilinophenyl) acrylamide under High Pressure" (Tanaka et al., 1977), "Thermal Decomposition of Tetraoctadecyl Titanate under Elevated Pressure" (Tomizuka and Tanaka, 1977), and "High Pressure Copolymerization of 2, 3-Epoxy-1-propyl Methacrylate with 2-Vinyl-5-ethylpyridine" (Tanaka et al., 1976).

In addition to carrying on similar studies, future plans here also call for efforts to make organic-semiconductors using explosive shock wave techniques to produce pressures in excess of 20 GPa. This effort will be started within the next few months in collaboration with Professor Akira Sawaoka of the Tokyo Institute of Technology (cf. Part II-X-2).

3. Polymer Physics

Drs. Hisaaki Kanetsuna and Kazuo Nakayama and their co-workers have been involved in studies of hydrostatic extrusion of crystalline solid polymers for many years. The work is pursued with the objective of describing the structural changes in plastics produced by hydrostatic extrusion and to characterize the physical properties of the extrudates in terms of the extrusion conditions.

The extrusion experiments are conducted in an hydrostatic-extrusion apparatus made by Kobe Steel, Ltd., and is operational to pressures of about 1 GPa. The billet (polymer rod to be extruded) is typically about 7 mm in diameter. Glycerin was used as the high pressure medium and the die angle and extrusion ratio* were variables in the research; extrusion ratios from 3 to 9 were examined and die angles between 20° and 120°. X-ray analyses were performed on the extrudates.

The work of this group has been reported in a series of papers (Nakayama and Kanetsuna, 1973, 1974, 1975, 1977, and 1978). Some of the conclusions they have arrived at include: (1) the minimum pressure required for extrusion decreases with increasing temperature; (2) at low extrusion ratios (<4), there was a pronounced reduction in the crystalline size, accompanied by a considerable degree of orientation; (3) at high extrusion ratios (>4) there was a continuous increase in the molecular orientation caused by motion of small crystallites in the extrusion direction; (4) at higher extrusion temperatures (70 to 110 C) the Vickers hardness number of polyethylene increased with increasing extrusion ratio. Moreover, Nakayama and Kanetsuna have determined that, in general, hydrostatic extrusion of solid polymers results in a drastic increase in the Young's modulus of the extrudate because of the order intro-

*The extrusion ratio is defined as the ratio of the cross-sectional area of the billet to that of the extrudate.

duced in the orientation of the molecular chains. They also conclude that it is important for both pressure and deformation to be exerted on the polymer in concert, i.e., either one applied alone will not yield the improved physical properties.

Work is continuing in this group with the philosophy that one means of developing new, supermolecular structures is by shaping of polymers in the solid state and that such research may lead to the realization of new polymers with better capabilities and added value. It is further hoped that new polymer processing methods will be developed, independent of the conventional melt-molding techniques of the past.

Other studies underway here include investigation of the crystallization and melting properties of polyethylene at elevated pressures. Maeda and Kanetsuna (1974, 1975, and 1976) have performed a series of experiments on polyethylene up to about 600 MPa and 250 C. Extended details of the phase diagram are deduced from their dilatometry, DSC and x-ray measurements.

Kataoka et al. (1976) are examining the effect of various filler materials on the extrudate in hydrostatic extrusion experiments. Current work involves the mixing of silas balloons and glass beads with the polymer before extrusion.

4. Summary

The high pressure research at RIPT represents an excellent example of cooperation between industry and science. There is some very fine research being pursued at RIPT with the basic objective of learning more about the effects of pressure and temperature on various solid state polymer reactions. The results of this research are leading to new and improved polymers which will ultimately find application in industry.

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U. RITSUMEIKAN UNIVERSITY (RU)

1. Introduction

Ritsumeiken University (RU) is a private school located in Kyoto not far from Kyoto University. The high pressure work underway here is concentrated in the Department of Chemistry and represents studies in four categories: (1) structure and molecular interaction of aqueous solutions, (2) kinetics and changes in enzyme and enzyme-like reactions, (3) structural changes in molecular crystals, and (4) the physical chemistry and structure of water in the liquid state.

2. Equipment

The types of measurements pursued with the aforestated objectives include: near-infrared and electron spectroscopy, NMR, viscosity, solubility, compressibility, and electrical conductivity measurements.

A variety of high pressure gear is currently in use: a clamp-type optical cell, fabricated from a cobalt alloy by the Mitsubishi Metal Mining Company, Ltd., is equipped with sapphire windows for spectrographic studies to 230 nm. Pressures to about 3 GPa are produced by a hydraulic pump and combined manganin and Bourdon gauge readings yield an uncertainty in the estimated pressure of about $\pm 2.7\%$ at 1.4 GPa. A similar clamp cell capable of pressures in the 0.6 to 1 GPa range is fitted with Be to provide an x-ray window of about $\pm 30^{\circ}$ in 2Θ. Using radiation produced in a Mo x-ray tube at 30 kV and 20 ma, useful diffraction data can usually be collected in two to three hours. A lever-type diamond-anvil cell has also been used for optical studies and work is presently underway to set up a new "Ken-ichi" cell for operation to 20 GPa (cf. Part II-Z-2a). In addition there are Bridgman-anvil facilities and various other pieces of standard high pressure gear. One item of note is a "stopped flow" pressure system for studying chemical reactions. Using a strain gauge on the outside of the reaction chamber, accurate assessments of pressure changes related to fast reactions can usually be made very quickly.

3. Research

A wealth of pressure related publications have emerged from this laboratory in recent years; some of the more interesting subjects include: "Studies on the Denaturation of Egg Albumen under High Pressure" (Suzuki, 1958) which begins with Bridgman's experiments in the 1930s of coagulating egg white at 400 to 500 MPa, "Effects of Pressure on the Helix and Random Coil Forms of Poly-D-glutamic Acid (Suzuki and Taniguchi, 1968), and "Effects of Pressure on Order-Disorder Transitions in Macromolecules" (Taniguchi, 1970).

One study in particular concerns the investigations by Suzuki and Tsuchiya (1975) of the effect of hydrostatic pressure on the hydrogen-bond formation between phenol and dioxane in n-hexane. Using the aforementioned clamp-type optical cell, the near-UV absorption spectra were observed under varying hydrostatic pressures to 148 MPa under conditions where the phenol concentration is very dilute. As the pressure was increased, the phenol-dioxane spectra shifted toward longer wavelengths and the amount of hydrogen-bonded phenol was observed to increase. Based on these data, the equilibrium constant for part of the reaction was determined and the volume change associated with the hydrogen bond formation estimated. This represents the first study of the effect of pressure on hydrogen-bond formation on the basis of UV absorption measurements.

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V. SUMITOMO ELECTRIC INDUSTRIES, LTD. (SEI)

1. Introduction

One of the larger installations of Sumitomo Electric Industries, Ltd., (SEI) is located on the Osaka Bay in the city of Osaka. This company was founded in 1897 for the purpose of manufacturing electric wire and cable and since that time there has been considerable diversification in the interests of SEI. This expansion of interests is reflected in their current R&D program which encompasses the following groups: Information Systems, Organic Materials, Metals and Inorganic Materials, and the Extra-High Voltage Research Laboratory.

2. Pressure Related Research

High pressure research activities at SEI are concentrated in two areas: hydrostatic extrusion of fine wires and synthesis of hard materials, e.g., BN. Work in the former area is pursued by Dr. Masanori Hinata and his co-workers. Over the past several years, they have developed an apparatus for hydrostatic extrusion in industrial applications. The extrusion machine called "Fluidraw" was developed by SEI in cooperation with the Saikawa Ironworks Company, Ltd., and the Riken Seiki Company, Ltd. The apparatus has the capability of operating at hydrostatic pressures up to 1.5 GPa and can produce an extruded wire in a continuous operation. In Fig II-V-1 results of extrusion pressure versus extrusion ratio for various wires and extrudate diameters are plotted. Some of the conclusions resulting from extrusion experiments here are that (1) the surface of the extruded wire can be made smooth with proper lubrication, (2) a very high reduction rate can be achieved (as compared to a maximum of about 30% for conventional wire drawing processes), and (3) using hydrostatic extrusion methods, it is possible to extrude wires which are difficult to draw by conventional methods, as well as those with complicated cross-sections (Matsuda et al., 1976).

Other high pressure work at SEI is focused on the synthesis of ultra-hard materials for ultimate use in grinding applications. Although details were not available, it was learned that a very hard boron nitride compound has recently been produced. It is referred to as "Sumiboron" and identified by the SEI label of BN200. Limited data sheets describing the properties of the material are available in Japan.

3. References

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W. TOHOKU UNIVERSITY (TU)

1. Introduction

The pressure related research at Tohoku University (TU) is carried out by three groups at the Research Institute for Iron, Steel, and Other Metals. This Institute is located at Sendai on the eastern coast of Japan about 300 km, or 184 miles, north of Tokyo. It is one of five such groups attached to TU. Here attention is focused mainly on metals but, in recent years, some work has also been done on certain oxides and carbides.

2. Structural Investigations

Professor Hiroshi Iwasaki and his co-workers are studying the effects of pressure on ordering in structures over long periods. Conventional x-ray diffraction data are recorded from quenched samples. These specimens are

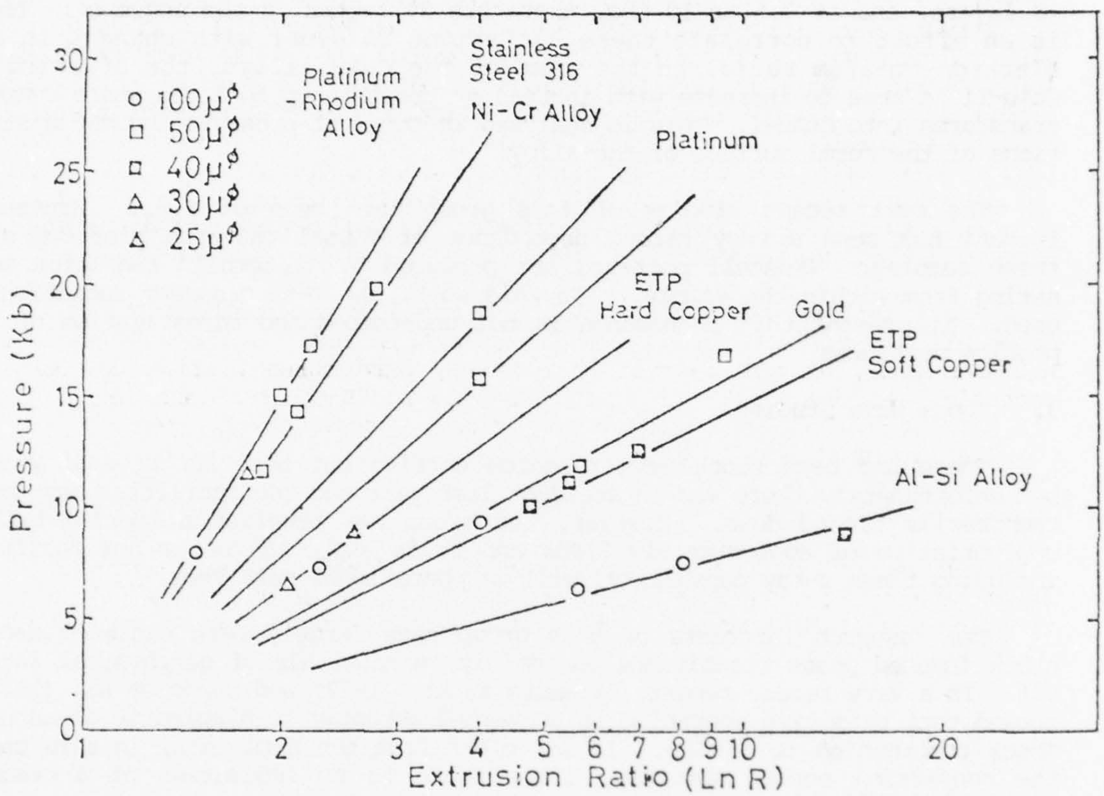

Fig. II-V-1: Extrusion pressure versus extrusion ratio for various materials (from Matsuda et al., 1976).

annealed for various time periods to pressures up to 7 GPa and temperatures to 500 C in a tetrahedral anvil press and to 10 GPa and 250 C in a Bridgman-anvil press.

Studies have been concluded on CuAu (Iwasaki et al., 1974a), Mg_3In (Iwasaki et al., 1974b) and Cu_3Pt (Iwasaki, 1974). Generally it is found that the ordering is increased as a function of annealing pressure--as an example, in Mg-24.1 at. % In at ambient pressure a long periodic stacking structure is observed with 12 layers; at 2.0 to 5.5 GPa, the sequence contains 18 layers; and at 7.5 to 10 GPa, there are 24 layers in the sequence. There is an effort to correlate these variations in order with changes in the electron-to-atom ratio. In the case of the CuAu alloys, the ordering of CuAu-II is seen to increase with increasing pressure up to 5 GPa where CuAu-II transforms into CuAu-I. This is analyzed in terms of pressure induced distortions of the Fermi surface of the alloy.

The most recent studies of this group have been of Y_2O_3. Professor Iwasaki has seen a very strong dependence of Kossel patterns produced with these samples. (Kossell patterns are produced by "internal" radiation emanating from within the sample.) In this work, the Y-fluorescent radiation is used. At present this phenomenon is not understood and investigation of the problem continues.

3. Shock Wave Studies

There had been shock wave research carried out here for several years, but unfortunately there was an accident last year and the facilities have been temporarily closed down. However, the group has received a special budget appropriation of approximately $100K and it is expected that a new facility, including flash x-ray capability, will be operational next year.

The research interests of this group have largely been centered around shock induced phase transitions and mainly in materials of geophysical interest. In a very recent report, Kitamura et al. (1977) and Syono et al. (1977a) showed that primitive anorthite is converted abruptly to diaplectic glass upon shock compression to 30 GPa. It was clear from the data that, in this case, the conversion occurs abruptly, i.e., there is no indication of a gradual change in the original domain size.

In another study, data were recorded during the shock compression by means of a streak-camera. The arrival times of multiple waves traveling through the specimen are recorded on a photographic film and the presence of phase transitions in the shocked specimen is deduced from the various wave velocities. The results of Syono et al. (1977b) and Goto et al. (1976) on Fe_3O_4 and GaAs show transitions at pressures significantly lower than the transition pressures obtained in static experiments. In the case of Fe_3O_4, a suggested explanation is the sluggish nature of the transition as seen in the static experiments, whereas for GaAs, it is suggested that the elastic-plastic model used, may not be applicable. The discrepancies remain, however, unresolved.

4. Magnetic Materials

The third group at TU is examining phase transitions in various magnetic materials. In addition to conventional high pressure electrical resistivity measurements, work is also underway to set up a neutron time-of-flight system at the Japan Atomic Energy Research Institute (cf. Part II-E-5). A WC-piston cylinder apparatus has been fabricated with an inner cylinder of TiZr and neutron windows at 30° and 90° in 2θ. The facility has a pressure limit of about 1.2 GPa and CS_2 is used as the pressure medium. As part of the initial testing, ambient pressure time-of-flight neutron diffraction patterns have been recorded on Al, steel, and NaCl. Most recently, high pressure NaCl patterns were also recorded.

This group has also investigated the effect of pressure on the Néel temperature in the system $CrSb_{1-x}As_x$ (Kaneko et al., 1977) and the insulator-to-metal transition in the system $Sm_{1-x}Gd_xS$ (Ohashi et al., 1977).

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X. TOKYO INSTITUTE OF TECHNOLOGY (TIT)

1. Introduction

The Tokyo Institute of Technology (TIT) has a history dating back to 1881 when it was created as a vocational school, Tokyo Shokko Gakko. Following a series of upgradings, TIT was elevated to full university status in

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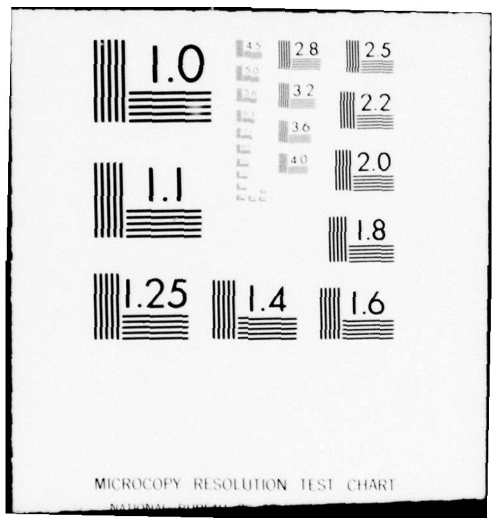
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1929. The graduate school, established in 1953, maintains campuses at Nagatsuta and Ookayama. The latter campus is located in the southwest suburbs of Tokyo and houses several major research laboratories, among which is included the Research Laboratory of Engineering Materials, directed by Dr. Shinroku Saito. This Laboratory is subdivided into eight divisions each including six to eight research personnel. Two divisions engaged in high pressure research are the Materials for Ultra-High Temperature Division headed by Professors Shinioku Saito* and Akira Sawaoka and the Synthetic Inorganic Materials Division under Professor Shigeyuki Sōmiya.

2. Materials for Ultra-High Temperature Division

The productivity of this Division in recent years has been very high; the work may be grouped into four categories: (1) boron nitride; (2) two-stage light gas guns and associated flash x-ray studies; (3) phase studies and other problems of general interest, and (4) sintering of metal powders by isostatic compaction.

a. Boron-Nitride

Work on boron nitride and other superhard materials has been underway in this group for several years now. Currently about one million dollars is being supplied by MITI through the Nippon Oil and Fats Company, Ltd., for synthesis of super-hard materials; about 1% of this funding is seen at TIT.

The earlier studies on boron nitride were focused on characterizations of the phase diagram. Using shock compression techniques to 55 GPa, Sōma et al. (1974a,b) and Sawaoka et al. (1974) transformed graphite-like BN (g-BN) into a mestastable wurtzite structure (w-BN). Further studies led to more accurate characterization of the phase diagram of the three BN phases: g-BN, w-BN, and the zinc blende type structure (z-BN) (Tani et al., 1975 and Sōma et al., 1976). These investigations were pursued in a cubic-anvil apparatus equipped for resistive heating to 2500 C and operational to pressures of about 7 GPa. The starting material consisted of both g-BN and w-BN, the latter form having been produced by shock compression methods by the Nippon Oil and Fats Company, Ltd.

A very striking feature of this work is the observation that w-BN transforms to g-BN in a region where z-BN is expected to be thermodynamically stable. Moreover, the high pressure produced g-BN can be converted to z-BN simply by an application of pressure.

The most recent development in this program is very exciting, viz., a sintered BN-compact with significantly superior mechanical properties (Sawaoka et al., 1977). W-BN previously produced by shock compression methods is transformed at elevated temperatures and under static pressure to the z-BN. A compact of this material sintered at 1450 C and 6.7 GPa yields a sample with both phases (w and z) present and distinctly superior properties; viz., a hardness slightly better than that of z-BN sintered directly from g-BN and a

*Professor Saito resigned his professorship on 31 March 1978 to accept the post of president of TIT.

threefold increase in the compressive strength (<2 GPa for z-BN produced from g-BN versus 6 GPa for z-BN produced from w-BN). Comparisons of the hardness and compressive strengths of several TIT produced BN-compacts are made in Table II-X-1.

Table II-X-1: Comparison of Hardness and Compressive Strenths of Several BN-Compacts

STARTING MATERIALS	SINTERING CONDITION P(kbar)	T(C)	DENSITY (g/cm^2)	PRODUCT	HARDNESS (kg/mm^2)	COMPRESSIVE STRENGTH (kg/mm^2)
fine grained g-BN	66.5	1430	3.49	z-BN	>7500	<200
shock-synthesized w-BN	67.0	1200	3.31	w-BN	2500	—
	67.0	1450	3.49	(w+z)-BN	7600	600
	67.0	1600	3.49	z-BN	6500	<200

At the forthcoming European High Pressure Conference, Sawaoka and Holzapfel will report the details of an experiment to use the superior z-BN as a pressure anvil. The arrangement shown in Fig. II-X-1 was used to produce pressures above 30 GPa. Following this, a microscopic examination of the BN-surface revealed a ~0.5μ indentation produced by the diamond. Current plans are to make a Bridgman anvil of the (w+z)-BN piece and attempt 50 GPa and higher pressures. One immediate advantage of this (w+z)-BN compact is that no binding material is used and the compact has roughly the same low x-ray absorption coefficient as diamond, thereby permitting straightforward x-ray studies in high pressure systems employing such BN anvils.

Another application currently under investigation involves potential use of sintered BN-compounds for cutting tools. Sawaoka readily admits that the GE Borazon product is superior to the BN-sintered at TIT for cutting tool applications, but current efforts involve introduction of 3 to 9% of TiB_2, ZrB_2 or HfB_2 for binding purposes. A superior product as viewed in terms of cutting applications also may be forthcoming shortly.

b. Gas-Gun and Flash X-Ray System

The development of a two-stage light gas gun with associate flash x-ray apparatus was started at TIT seven years ago for the purpose of studying the physics and chemistry of shock compressed solids. The system is patterned after the facility at Lawrence Livermore Laboratory and a preliminary report on its construction was given at the 4th International Conference on High Pressure in Kyoto (Konda et al., 1974). The gun is of the "accelerated-reser-

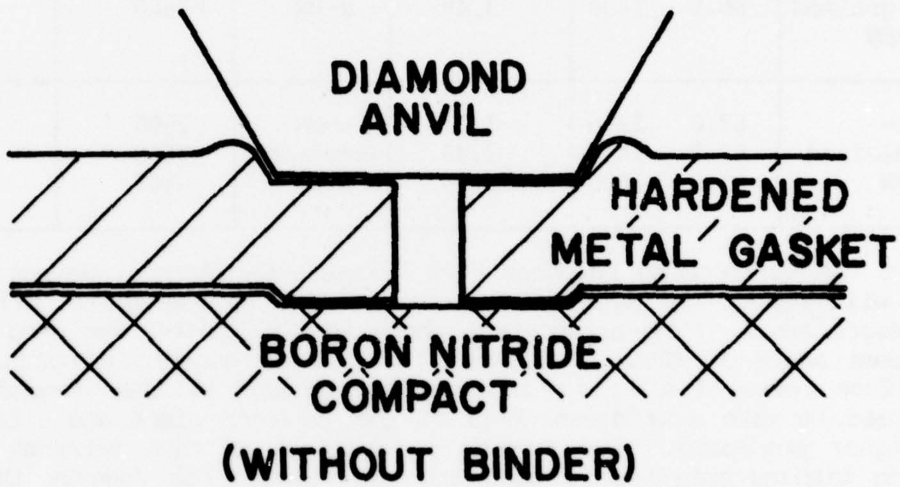

Fig. II-X-1: Schematic drawing of testing arrangement of BN-compact as possible ultra high pressure anvil material.

voir" type and has a bore diameter of 15 mm. Initially the muzzle-velocity was less than ~4 km/sec, but more recent advances have yielded maximum velocities of 6 km/sec. Details of the design and construction of this facility may be found in the paper by Sōma et al. (1974c). At present an improved gas gun is under construction which is expected to have an upper velocity limit approaching 8 km/sec. It will also employ up to three x-ray tubes for very accurate velocity measurements.

The flash x-ray diffraction system is designed to provide structural data within the period of the shock experiment. The system presently operating at TIT can produce an x-ray pulse of less than 80 nsec with at a charging voltage of 35 kV. Using an improved focusing method and an image intensifier, the uncertainty in diffraction angle (2θ) is estimated to be about 1^o at 40^o. The details of this system are discussed in the papers by Kondo et al. (1975, 1977a). In addition, in a method similar to that used at California Institute of Technology, electrical resistivity data can also be recorded during passage of the shock pulse.

The first major investigation made with this facility at TIT has been of single and polycrystalline LiF to shock pressures of 50 GPa (Kondo et al., 1977b). Preliminary results from this experiment indicate that the in situ (flash x-ray) crystalline volume is systematically smaller than that associated with the Hugoniot curve. Moreover, it was found that the linear compressibility was greater in the <111> direction than in the <100> direction.

Until recently, researchers at TIT have had serious problems with tilting of the projectile during flight, but these difficulties have now been overcome and additional studies are underway.

c. Phase Studies and Related Problems

In addition to the facilities referenced above, other high pressure systems include a Bridgman-anvil apparatus for work up to 10 GPa, a cubic-anvil apparatus equipped for in situ x-ray studies at up to 11 GPa, and a piston-cylinder girdle-type system capable of pressures to 6 GPa and temperatures to 1000 C. The piston-cylinder apparatus can be used for DTA, ultrasonic, and 4- or 6-lead electrical measurements. Investigations involving these facilities and completed within recent years include the following: melting curves of AgCl, AgBr, $AgNO_3$, and Bi_2O_3 (Saito and Ozaki, 1970); electrical conductivity in ceria-zirconia solid solution at high temperatures (Okikawa et al., 1970); ionic conduction in Na-β-alumina (Itoh et al., 1975); pressure dependence of the Néel temperature of γ-Mn (Sawaoka et al., 1971), crystal growth of brucite (Yamaoka and Saito, 1971); order-disorder transitions and melting curves of Mg-Cd alloys (Akaishi and Saito, 1973a,b) and S-VMn alloys (Suzuki et al. 1975); and phase studies of the following systems: FeS_2, CoS_2 (Sawaoka et al. 1974), and Bi-As alloys (Akaishi et al., 1974). Most recently the melting curve of Pb has been determined to pressures above 7 GPa for high pressure-high temperature calibration (Akaiashi et al., 1977).

A very recent investigation undertaken in this laboratory by Dr. Kenichi Kondo concerns the possibility of a phonon mode softening in fused quartz.

Ultrasonic measurements of the pressure dependence of the elastic moduli have revealed minima at about 2.2 GPa in both the transverse and longitudinal waves. The shear, bulk, and C_{11} elastic moduli all show a characteristic monotonic decrease with increasing pressure up to 2-2.5 GPa, above which there is an anomalous increase in these moduli (Fig. II-X-2). The details of this phenomenon are currently under investigation of TIT.

d. Sintering of Metal Powders by Isostatic Compaction

Another area of high pressure materials research in this group involves isostatic sintering studies. In one case, Saito and Sawaoka (1973) studied a fast sintering process which they refer to as "spark isostatic pressing." The idea being that, on passage of a substantial electrical current through the compact (the electrical path being highly pressure dependent), the oxide layer on the respective particles is broken down by the electrical spark, thus yielding a fast bond formation. In another study Sawaoka and Saito (1974) developed a hot isostatic compaction process in which molten glass was used as the pressure transmitting medium. This facility was used to produce a manganese zinc ferrite ($(Mn_{0.8}Zn_{0.2})\ Fe_2\ O_4$) compact with a density equivalent to the microscopic value. Ozaki and Saito (1973, 1974) have used isostatic pressing techniques to make ceramic joints; it was found that above a certain reaction pressure, the strength of the joined body is equivalent to that of a uniform body.

3. Synthetic Inorganic Materials Division

A large portion of the high pressure research pursued in this division centers around the many Hikkiso high temperature hydrothermal reaction chambers available: 24 with a 5.5 cm^3 volume, 4 at 27 cm^3, 3 at 150 cm^3 and 3 at 250-500 cm^3. These units are capable of pressures approaching 350 MPa and temperatures to 1800 C. In addition there are two piston-cylinder rigs with P,T capabilities of 1 GPa and about 1500 C, respectively, with a 5.5 cm^3 sample volume.

Some of the single crystals grown in these facilities include the following: ZrO_2 at 650 C and about 150 MPa stabilized with Y_2O_3 (Nakamura et al., 1977); Fe_3O_4 in the presence of hydrogen (Hirano and Sōmiya, 1976a); brucite ($Mg(OH)_2$) (Nakamura et al., 1976a and 1975a); sodium iron titanium bronze compounds (Nakamura et al., 1976b), In addition phase relations in the following systems were examined ZrO_2-Y_2O_3 (Nakamura et al. 1975b) and Cr_2O_3-MgO-TiO_2 (Sōmiya et al., 1977) and decomposition of ilmenite in KOH-H_2O solutions under elevated pressure (Ismail et al., 1974 and Hirano et al., 1976).

Quite recently Hirano and Sōmiya (1976b) have developed a new hydrothermal reaction sintering method to fabricate pure, high density Cr_2O_3 without any additive. At 500 C and about 100 MPa, the following reaction produced fine-grained, active chromium oxide:

$$2\ Cr + 3\ H_2O \rightarrow Cr_2O_3 + 3\ H_2$$

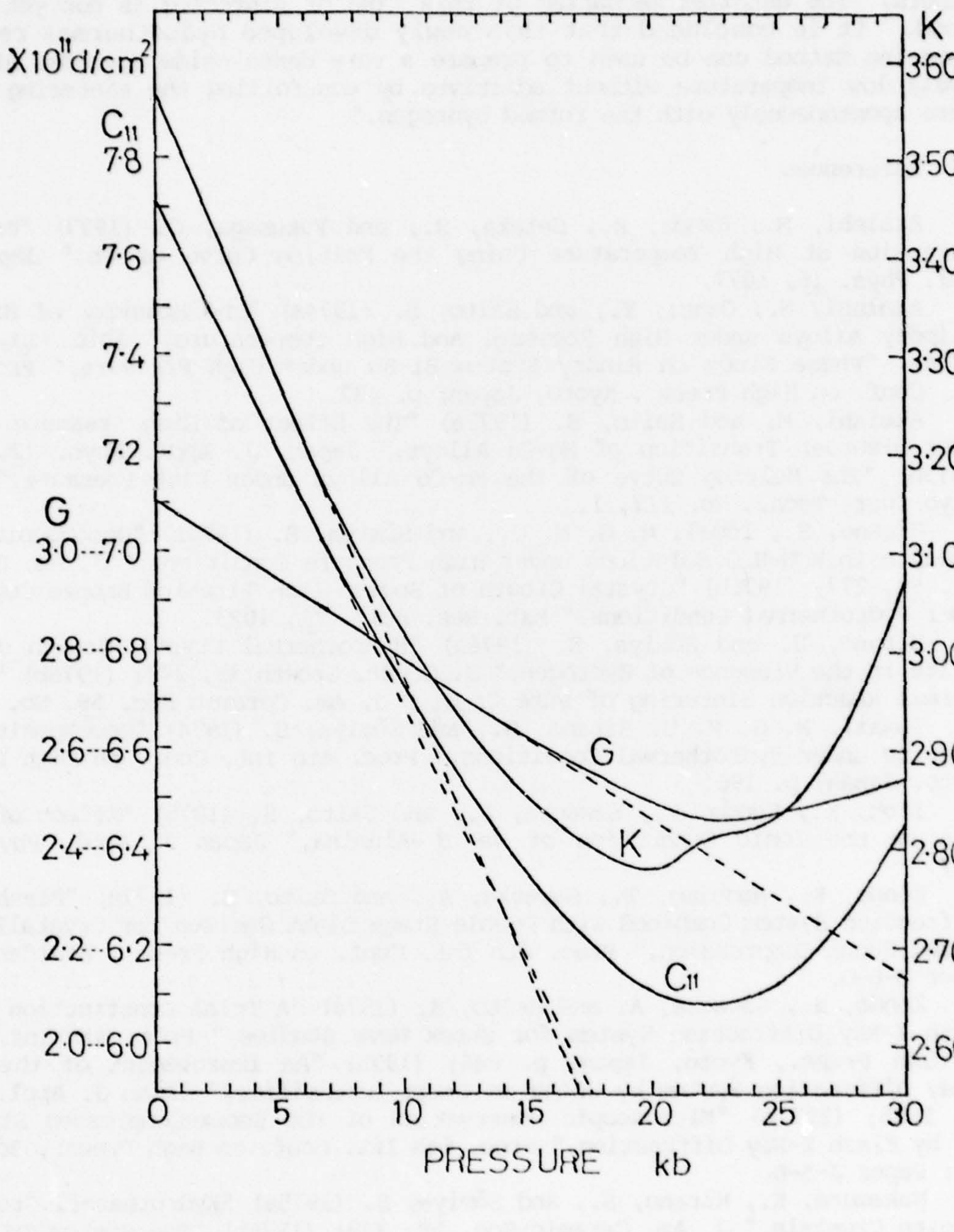

Fig. II-X-2: Pressure dependence of the shear (G), bulk (K) and elastic stiffness (C_{11}) moduli for fused quartz (unpublished data of Dr. Kondo).

By increasing the reaction temperature to 1000 C, a Cr_2O_3 product is obtained with a measured density 99.2% of the theoretical value. In the words of the authors, "The detailed mechanism of this kind of sintering is not yet understood. It is concluded that this newly developed hydrothermal reaction sintering method can be used to prepare a very dense oxide specimen at relatively low temperature without additives by controlling the sintering atmosphere spontaneously with the formed hydrogen."

4. References

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Y. TOKYO SHIBAURA ELECTRIC COMPANY, LTD. (TOSHIBA)

1. Introduction

Research appertaining to the development of high pressure apparatus and ultra hard materials had been supported by the Tokyo Shibaura Electric Company through the Toshiba Research and Development Center in Kawasaki. At present, high pressure research at Toshiba is being phased out and the high pressure laboratory is closed; an on-site visit was not possible, but information was exchanged with Dr. Masao Wakatsuki. It was learned though, that plans are underway to produce comercially a diamond-anvil pressure cell, viz., the "Ken-ichi cell" designed by Professor Minomura et al. of The University of Tokyo (cf. Part II-Z-2a).

2. High Pressure Apparatus

In past years, Toshiba had been instrumental in developing and marketing a cubic anvil apparatus. Actually there are several companies involved in the patent documents of this appratus: in addition to Tokyo Shibaura Electric Company, Ltd., there is Toshiba Tungalloy Company, Ltd., and Ishikawajima-Harima Heavy Industries, Company, Ltd. (IHI). The latter company is actually involved in production of this gear and most of the presses bear the "IHI" trademark.

A cubic-anvil apparatus is also marketed by Kobe Steel Company, Ltd. In the Kobe-cubic press, the load obtained from the uniaxial hydraulic ram is converted into multiaxial components by means of a wedge-like action on Teflon covered tapered surfaces (cf. Part II-G-2). The IHI-press, however, is based on the original design of Tsujii et al. (1967) which uses a link-structure to convert a uniaxial force to multiaxial components. The press has two vertical and four lateral anvils arranged in a cubic configuration. There are support blocks for the upper and lower anvils which are connected by movable arms or links to the four lateral anvils. The maximum pressures obtainable in the assembly depends, of course, on the volume of the pressure cavity: 10 GPa with 10 mm edge anvils; 12 GPa with 6.4 mm anvils. A cross-section of the assembly is showed in Fig. II-Y-1 and complete details are given by Wakatsuki et al. (1971). Provisions are also made for heating the pressure chamber to 2000 C; at this value, the temperature of the anvils does not exceed 300 C.

Some efforts were also expended in consideration of appropriate gasket materials. Consideration of various materials was made by Wakatsuki (1965) and an examination of the use of a compressible gasket in a Bridgman-anvil apparatus (Wakatsuki et al., 1972a).

3. Super-hard Materials

Work has also been pursued at Toshiba on the high pressure synthesis of both diamond and boron nitride. The diamond studies centered on evaluation of catalysts: Wakatsuki (1966) attempted using transition-metal elements alloyed with various noble metals. Conditions for diamond synthesis were found to be basically the same as for the catalytic agents previously used. Subse-

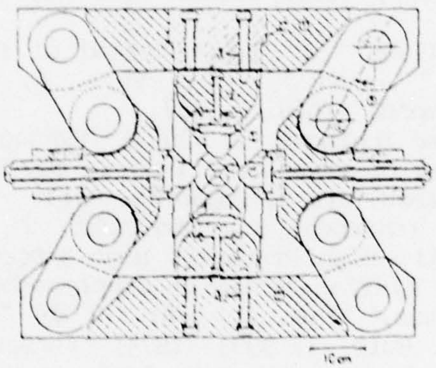

Fig. II-Y-1: Schematic drawing of cubic link-type high pressure apparatus (from Wakatsuki et al., 1971).

quent studies were pursued by Wakatsuki et al. (1974) on the use of Cu and Cu alloyed with both TiC and Nb as catalysts. An optimum yield was generated with roughly a 50-50 mol-% TiC and Cu alloy.

Studies were also completed on high pressure synthesis of BN (Wakatsuki et al., 1972b; Ichinose et al., 1974; Wakatsuki and Ichinose, 1974). The conclusions reached were that (1) hexagonal-BN with both low structural ordering and smaller crystallite sizes can be converted to the cubic-form at a lower pressure, (2) the presence of moisture lowers the (P,T)-conditions necessary for conversion, and (3) the use of well-crystallized starting materials leads to direct conversion to the wurtzite-form, whereas poorly crystallized starting materials leads to the cubic-form. This latter conclusion is attributed to diffusionless and diffusion-like mechanisms of the phase transformations, respectively.

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Z. THE UNIVERSITY OF TOKYO (UT)

1. Introduction

The University of Tokyo (UT) continues today as the most prestigious and renown of all the Japanese universities. It is of course not surprising to find an abundance of pressure related research underway at UT. This work is divided between the Mineralogical and Geological Institutes located on the main campus at Hongo and the Institute for Solid State Physics (ISSP) at Roppongi. Both sites are accessible from virtually anywhere in Tokyo within an hour via the excellent Tokyo subway system.

2. Institute for Solid State Physics (ISSP)

The Institute for Solid State Physics (ISSP) was created more than twenty years ago for the purpose of providing Japan with high quality research facilities which would be competitive with those in the United States, western Europe, and the Soviet Union. In the ensuing years, numerous Japanese universities have also developed excellent research laboratories and the mission of the ISSP has recently been redefined.

Today the ISSP seeks to provide a seat of expertise in a few specific experimental research areas, among which are ultra-high magnetic fields, surface studies, crystallography, ultra-low temperature physics, and high pressure science. Some groups have already received funding for major upgradings: for example, the ultra-low temperature, or micro-Kelvin, group, as it is commonly called, was allocated $1.5M over the past three years. As a consequence of this, there are now five dilution refrigerators in operation at the ISSP, one of which is set up for thermodynamic studies on $L\text{-}He^3$ and capable of temperatures down to 1 mK.

The high pressure groups have not as yet received any major financial grants, nevertheless, significant improvements have recently been realized on a well established and formidable base. The high pressure work at the ISSP can be roughly divided into three general areas: solid state physics under Professor Shigeru Minomura, low temperature studies under Professor Genshiro Fujii, and geophysical studies under Professor Syun-iti Akimoto.

a. High Pressure Equipment

a(1). Diamond-Anvil Cell:

There is an abundance of unique and sophisticated high pressure research equipment in use at the ISSP. At the top of the list perhaps stands what appears to be the first and, so far, only diamond-anvil pressure cell in operation in Japan which is solely of Japanese design and construction. Takemura et al. (1977) have recently produced pressures in excess of 20 GPa in this diamond-anvil cell which is a modified version of those in use in both the U.S. and Europe; the Japanese cell is called the "Ken-ichi model" (Fig. II-Z-1). (One modification is in the diamond alignment mechanism: As shown in Fig. II-Z-1, alignment of the diamond anvils can be made without removing either of the anvil assemblies simply by adjusting the upper support plate from the outside. This results in a very rapid alignment and set up operation. Moreover a ball bearing mechanism has been introduced to reduce the friction encountered in transferring the load from the diving screw to the piston assembly. Considerations are now being given to reducing the four alignment screws to three.

Takemura et al. (1977) have also given consideration to the pressure distribution in the cell. Based on ruby fluorescence measurements, the distribution produced to 20 GPa with the commonly used 4:1::methanol:ethanol hydraulic fluid mixture has been compared with that produced in e.g., an iodine medium. It was found that, at 20 GPa, with I_2, the variation in

pressure from the cell center to the periphery of the gasket was only about ±5% whereas the alcohol mixture showed a variance almost twice this amount (Fig. II-Z-2). The recommendation is that an appropriate pressure medium should be selected for the pressure range of interest.

As shown in Fig. II-Z-1, the driving screw is direct-acting, i.e., aside from the small deformation of the piston assembly on compression, the displacement of the moving diamond anvil is equal to the advance of the load screw. This group at ISSP has made an effort to correlate this motion with the pressure developed in the gasketed cavity. The graph in Fig. II-Z-3 is a plot of the angular twist of the load screw versus the measured pressure. In the case of a properly aligned gasket/diamond assembly, an approximately linear relation is seen (upper curve), whereas gasket rupture is preceeded by a pronounced loss in pressure in the case of poor alignment (lower curve). This catastrophic failure is also forecasted by an enlargement in the diameter of the pressure cavity.

The mechanical properties of gasket material being used here are similar to those used in western laboratories. Specifically, Udimet-700, a high strength Japanese metal, not unlike Inconel X-750 or Rene 41, is routinely employed. The gasket hole is produced by spark erosion down to about 0.1 mm diameter; the starting gasket thickness is typically about 1.5 mm.

a(2). X-Ray Measurements:

Just as is the case with the high pressure gear, there is also a large variety of x-ray apparatus available for use at the ISSP. In addition to conventional diffraction apparatus, including photographic and NaI(Tl)-detector, there is a Ge(Li) solid state detector (SSD) in service and plans are underway to set up a position sensitive proportional counter (PSPC). Each of these facilities can be operated in conjunction with the diamond-anvil pressure cell.

The SSD set up can be used in either the angular dispersive or the energy dispersive mode: Fukamachi et al. (1978) have fixed the position of their detector, but mounted the x-ray tube on one circle of a two-circle diffractometer. The system can then be operated either as a conventional diffractometer, by sweeping 2θ with the tube and monitoring the scattered radiation in selected channels or energy windows, or alternately, by fixing 2θ and recording the diffraction pattern as a function of energy; the equivalent information can be recorded somewhat more rapidly.

In collaboration with Professor Yamada and his co-workers at Osaka University, this group has also carried out high pressure x-ray measurements with a PSPC. The operation of this comparatively new detection facility is described in Part II-S-4b. Based on measurements with a PSPC using krypton and methane gas, Shimomura et al. (1978) estimate an x-ray counting efficiency of about 15% and for their recent studies on iodine, to 20.6 GPa; they offer the following comments: "With this PSPC system, the measuring time was reduced by a factor of about 10 compared to the step-by-step measurement using a conventional counter or a photographic method. The PSPC system supplied

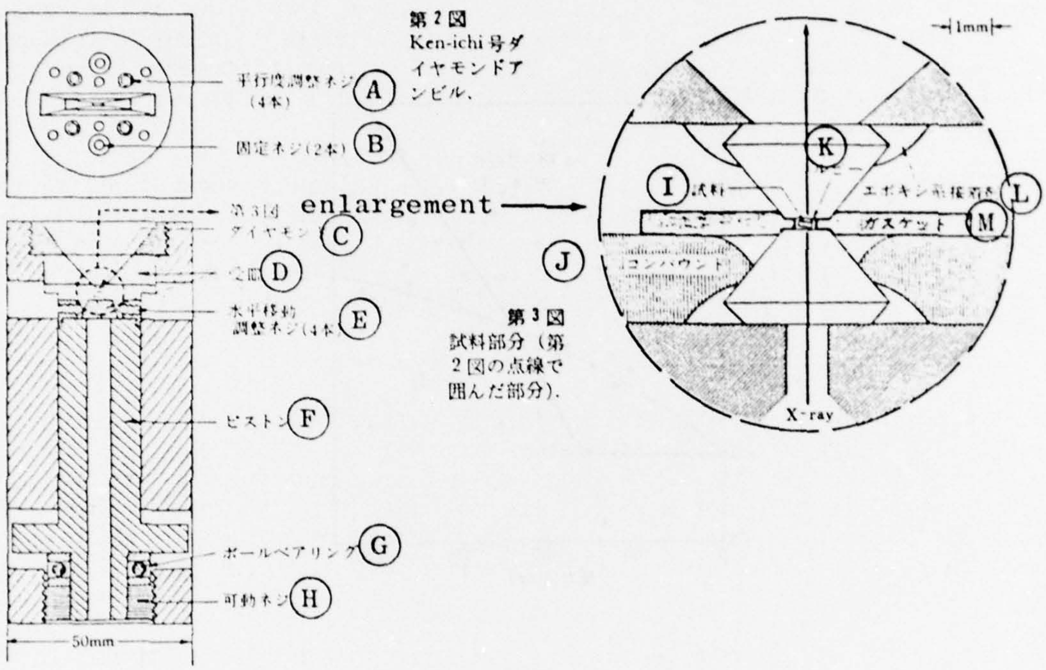

Fig. II-Z-1: Ken-ichi model diamond-anvil cell: A - parallelism adjustment screw (4 screws); B - setting screw (2 screws); C - diamond anvil; D - support saucer; E - horizontal adjustment screw (4 screws); F - piston; G - ball bearing; H - piston thrust screw; I - sample; J - gasket support compound; K - ruby chip; L - epoxy-based adhesive; M - hardened metal gasket (from Takemura et al., 1977).

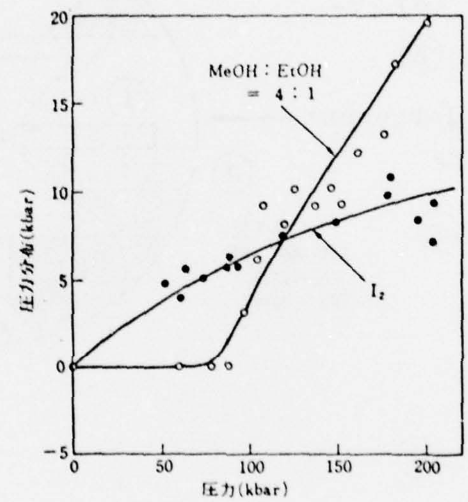

Fig. II-Z-2: Pressure distribution in Ken-ichi cell; plot shows the differences in pressure between the center of the cell and the periphery of the gasket (ordinate) as a function of the mean cell pressure (abscissa). The pressure values are estimated from the mean value of the half-width of the ruby fluorescence curve. Open circles correspond to a 4:1:: methanol: ethanol pressure medium; solid circles correspond to an iodine pressure medium (from Takemura et al., 1977).

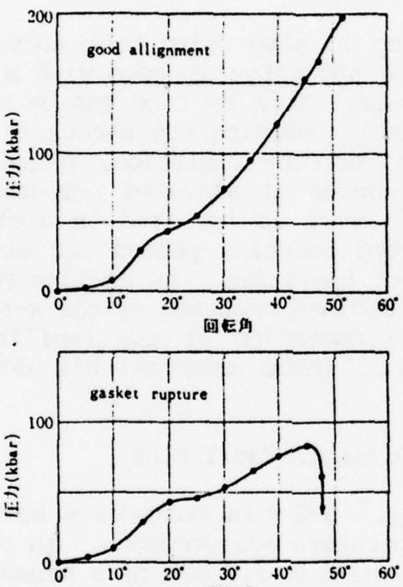

Fig. II-Z-3: Plot of the pressure developed in the Ken-ichi cell versus the angular rotation of the piston thrust screw (H in Fig. II-Z-1) for the case of good gasket alignment (upper curve) and gasket rupture (lower curve) (from Takemura et al., 1977).

data of better quality than the conventional method because (the) natural background of the PSPC was about 1/10 of the conventional method." The PSPC diffraction pattern of iodine at 20.6 GPa is shown in Fig. II-Z-4.

In response to questions about data collection time, the following information was obtained for the iodine study: using conventional methods (a Mo x-ray tube operated at 40 kV and 20 ma, and a 0.1 mm incident beam collimator) about one week (continuous operation) was required (three to four days with a 0.2 mm collimator); using the SSD about 50 hours are needed; the PSPC-pattern shown in Fig II-Z-4 was recorded in about 30 hours (3 steps of 10° each).

In the opinion of this author, the PSPC system is certainly exciting, but it has not been clearly demonstrated to be superior or inferior to the SSD in general operation. A definitive test of this issue would be helpful.

Professor Akimoto's group is also using both conventional and SSD x-ray equipment. In this case, the apparatus is used with a cubic anvil apparatus and a rotating anode x-ray tube. This Mo tube can be operated at up to 55 kV and 160 ma thereby significantly reducing the necessary data collection time. Because of this very intense incident radiation, x-ray data can be collected through pyrophllite gaskets--hence at elevated temperatures also. The diffractometer attached to this press is operated in a step-scan mode at 0.01° per step and a 5 to 10 second counting period per step; thus a 2θ-scan of 30° requires about 10 hours of operation. An on-line minicomputer is coupled to this facility to permit immediate analyses of the x-ray data. A Si(Li) SSD is presently in use and the operation of the facility is similar to that described in Part II-G-4 (Dr. Inoue received his doctorate under Professor Akimoto).

a(3). Low Temperature-High Pressure Facilities

Professor Genshiro Fujii and his coworkers have developed two high pressure systems for low temperature measurements. In one case, a piston-cylinder apparatus is operated to about 1.7 GPa by a manually activated oil pump operated at room temperature. The cell is designed to be operated in a liquid He cryostat and temperatures to 2K; the pressure can be varied at fixed temperatures. Both electrical resistance and magnetic susceptibility measurements can be made in this system (Fujii and Nagano, 1971).

In a second system, Fujii et al. (1972) designed a small Bridgman anvil apparatus for clamped operation in a variable temperature liquid He Dewar. The anvils are driven together in a hydraulic press at room temperatures, then clamped and immersed in the cryogenic environment. Both electrical phase transitions and the pressure dependence of superconductive transition temperatures can be measured with either a.c. susceptibility or d.c. resistance methods to pressures approaching 10 GPa and temperatures below 1K.

More recently, Fujii et al. (1974) have modified the aforementioned Bridgman anvil apparatus for operation in a dilution refrigerator. Thus measurements similar to those referenced above can be carried down to about 30

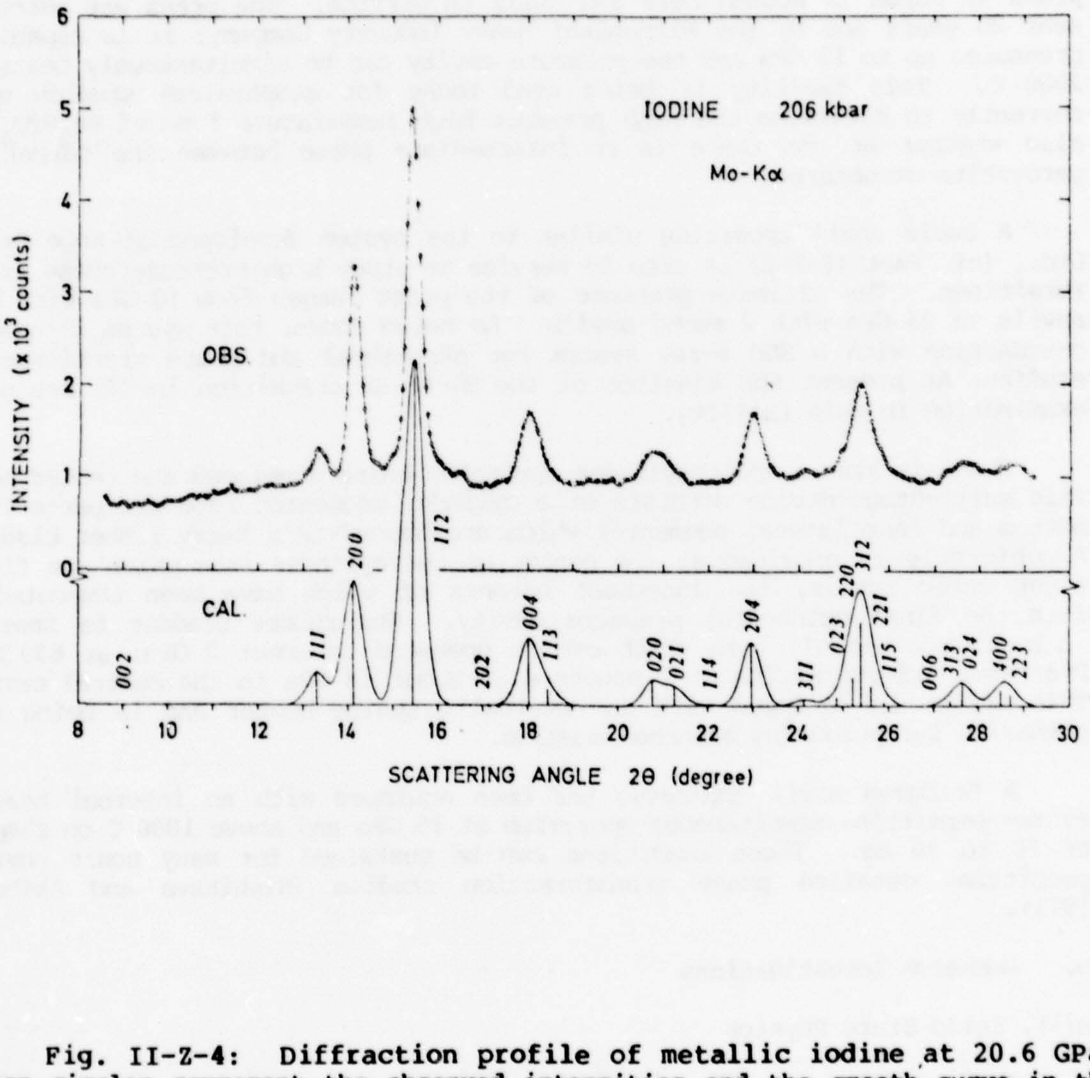

Fig. II-Z-4: Diffraction profile of metallic iodine at 20.6 GPa. Open circles represent the observed intensities and the smooth curve in the lower part of the figure is calculated based on the Cmca-space group. The indices of the appropriate Bragg reflections are given in the lower part of the figure (from Shimomura et al., 1978).

mK. Schematic diagrams of these low temperature clamp cells are shown in Fig. II-Z-5 and of the electrical connections for the d.c. resistance measurements in Fig. II-Z-6.

a(4). Hydraulic High Pressure Apparatus:

The large scale hydraulic gear at UT is no less impressive than the other exotic gear in use here: operated primarily by Professor Syun-iti Akimoto and his staff, there is perhaps an example of each type of modern high pressure apparatus in operation. What is said to be the first tetrahedral press in Japan is housed here and still in service. The press was assembled over 20 years ago by the Mitsubishi Heavy Industry Company; it is capable of pressures up to 12 GPa and the pressure cavity can be simultaneously heated to 2000 C. This facility is being used today for geophysical studies e.g., currently to determine the high pressure-high temperature form of Fe_2SiO_4 and also whether or not there is an intermediate phase between the garnet and perovskite structures.

A cubic anvil apparatus similar to the system developed at Kobe Steel, Ltd., (cf. Part II-F-2) is also in service to study high pressure phase transformations. The ultimate pressure of the press ranges from 10 GPa with 6 mm anvils to 23 GPa with 2 mm-WC anvils. As noted above, this system is used in conjunction with a SSD x-ray system for structural and phase transformation studies. At present the kinetics of the B1-to-B2 transition in KCl are under examination in this facility.

There is also a split-cylinder apparatus being developed and tested here. This multi-stage device consists of a cylinder segmented into six parts (top, bottom and four lateral segments) which are housed in a heavy rubber bladder. A cubic hole is provided at the center of the cylinder into which are fitted eight cubic anvils, the innermost corners of which have been truncated to form the final octahedral pressure cavity. The rubber bladder is immersed in a pressurized oil bath which can be operated to about 2 GPa; at 830 MPa, Professor Akimoto estimates a pressure of about 18 GPa in the central cavity. This system is equipped with an internal graphite heater and is being used primarily for producing quenched samples.

A Bridgman anvil apparatus has been equipped with an internal heating system permitting simultaneous operation at 15 GPa and above 1000 C on samples of 10 to 20 mg. These conditions can be sustained for many hours thereby permitting detailed phase transformation studies (Nishikawa and Akimoto, 1971).

b. Research Investigations

b(1). Solid State Physics

The pressure related research underway in Professor Minomura's group ranges from measurements of the melting curves of n-paraffin and polyethylene (Hikosaka et al., 1975a and b) to extended x-ray absorption fine structure (EXAFS) studies on Ni. Between these two extremes, much work has been done on

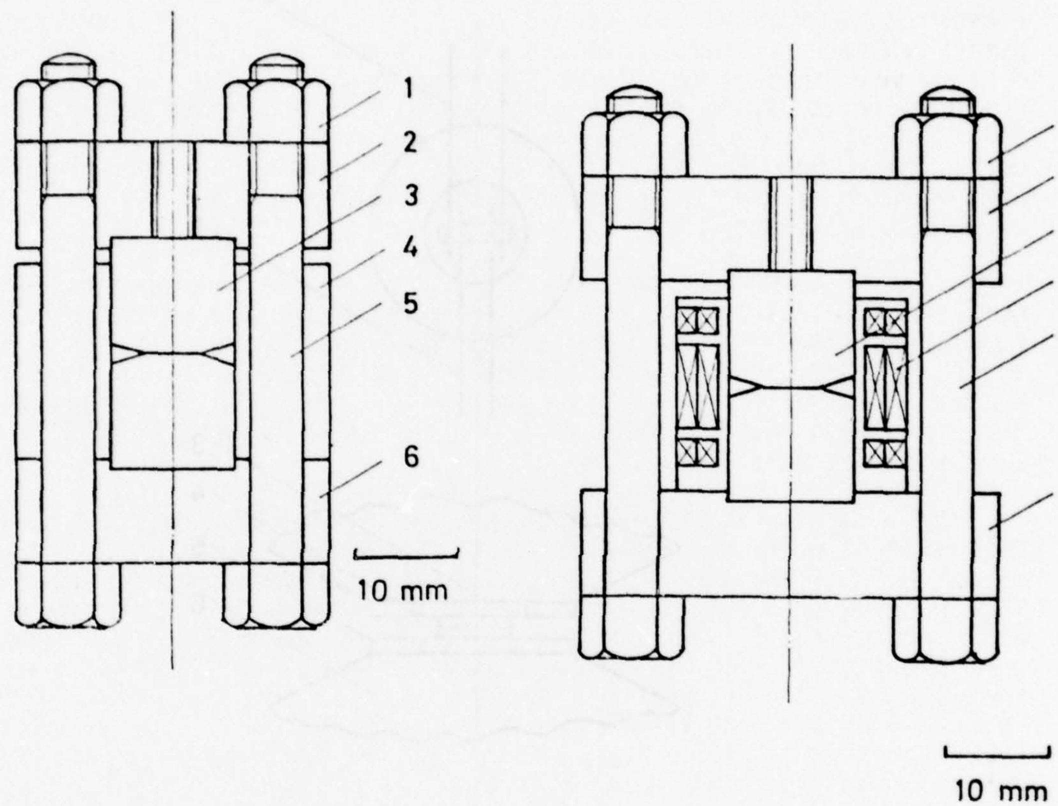

Fig. II-Z-5: Schematic diagram of low temperature Be-Cu clamp cell. Cell on the left-hand side is used for d.c. electrical resistance measurements. The numbers on the figure are identified as follows: 1 - fixing nut; 2 - upper flange; 3 - tungsten carbide anvil; 4 - anvil guide; 5 - fixing bolt; 6 - lower flange. The cell on the right-hand side is used for a.c. magnetic susceptibility measurements. The numbers on the figure are identified as follows: 1 - fixing nut; 2 - upper flange; 3 - tungsten carbide anvil; 4 - measuring coil; 5 - fixing bolt; 6 - lower flange (from Fujii et al., 1974).

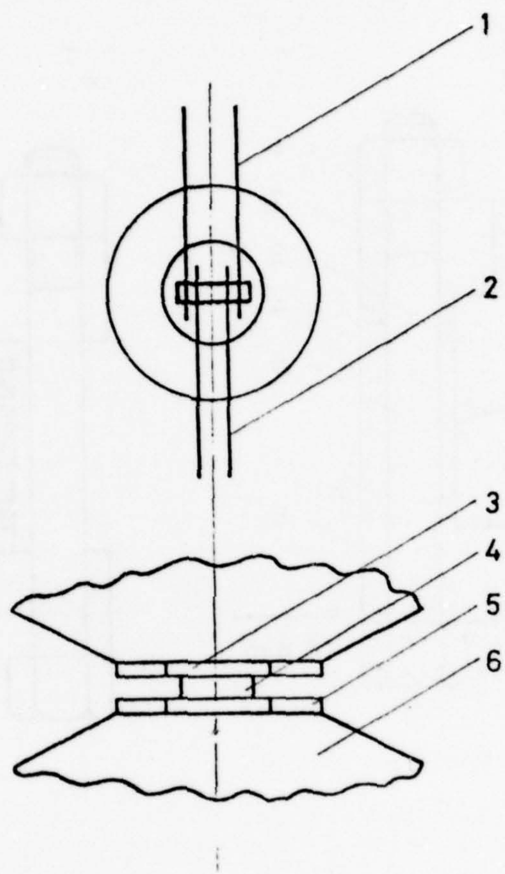

Fig. II-Z-6: Sample assembly for d.c. electrical resistance measurement made in the cell shown in Fig. II-Z-5. The numbers in the figure are identified as follows: 1 - current lead; 2 - potential lead, 3 - talc disk, 4 - sample, 5 - pyrophyllite ring, 6 - tungsten carbide anvil (from Fujii et al., 1974).

pressure-induced semiconductor-to-metal transitions--particularly in amorphous InSb (Asaumi et al., 1976 and Shimomura et al., 1976) and other III-V compounds (Minomura, 1977 and Minomura et al., 1977). In the work on amorphous Si and Ge, it was learned that each undergoes a semiconductor-to-metallic transition, Si at 10 GPa and Ge at 6 GPa. The transition in Si is reversible whereas Ge converts to a crystalline diamond-type structure. Moreover, both metallic phases exhibit superconducting transitions, at 9.9 K for amorphous Si and at 7.3 K for amorphous Ge. These may be compared with 6.70 K and 5.35 K, respectively, for the crystalline forms. The reasons for the enhanced transition temperatures with increase in disorder remains unclear. Similar studies were carried out on InSb, while pressure dependent Raman spectra were recorded with the diamond-anvil pressure cell for trigonal Se and Te (Minomura et al., 1977).

Two very current efforts include a structure analysis of the metallic phase of iodine (Shimomura et al., 1978) and the aforementioned EXAFS study of Ni. In the case of iodine, the initial data from this group indicate no change in the structure to 20.6 GPa, well into the metallic phase (Fig. II-Z-4). Efforts to measure the superconducting transition temperature of metallic iodine have not shown a superconducting transition down to 1 K.

EXAFS is a comparatively new material diagnostic tool which permits direct evaluation of interatomic spacings and atomic vibrational parameters from x-ray measurements of the absorption edge. These parameters are, of course, very sensitive to pressure and thus pressure dependent EXAFS measurements provide useful compressibility data which can be compared with conventional crystallographic data. This technique does however require a very intense source of continuous x-radiation such as that produced by a synchrotron. At present, a student from the ISSP is performing EXAFS measurements on Ni with a diamond cell at the Stanford Synchrotron Radiation Laboratory.

b(2). Low Temperature Measurements

Fujii et al. (1977) have recently measured both the pressure and temperature dependence of the electrical conductivity of the charge-transfer salts N-methyl-phenazinium-TCNQ and Rb-TCNQ to 10-12 GPa. No conductive maximum was observed in NMP-TCNQ to 10 GPa; anomalous electrical conductivity, however, was observed in Rb-TCNQ, although no insulator-to-metal transition was seen to 10 GPa.

b(3). Research in Geophysical Problems

Sato et al. (1975) have studied the relation between hysteresis in pressure-volume data and inhomogeneities in the sample. This work was performed on MgO, MnO, LiF, and NaF up to 8 GPa and referenced to the NaCl pressure scale. Yagi and Akimoto (1976a) calibrated transitions in Pb, ZnS, and GaAs against the NaCl scale; values were 14.2 $\pm$ 0.3 and 11.1 $\pm$ 0.2 for Pb, 16.2 $\pm$ 0.4 and 11-10 for ZnS, and 19.3 $\pm$ 0.5 and 11.5-10.0 for Ga As, for increasing and decreasing loads, respectively (all values are in GPa).

Other recent high quality geophysical studies of this group include a direct determination of the coesite-stishovite transition (Yagi and Akimoto, 1976b), investigation of the hydrostatic compression of the ilmenite phase of $ZnSiO_3$ and $MgGeO_3$ (Sato et al., 1977) and an examination of pyroxene-garnet solid solution equilibria in the systems $Mg_4Si_4O_{12}$ — $Mg_3Al_2Si_3O_{12}$ and $Fe_4Si_4O_{12}$ — $Fe_3Al_2Si_3O_{12}$ at high pressures and temperatures (Akaogi and Akimoto, 1977).

3. Mineralogical Institute

The high pressure research underway at the Mineralogical Institute of UT is somewhat limited at present, but scheduled for immediate growth. The group is headed by Professor Takeuchi and has interests related to mineralogical studies with current emphasis on selected silicates and oxides. The group is extremely well equipped to measure electron density maps and characterize appropriate crystallographic properties, e.g., super-lattices. (X-ray equipment housed here includes five precession cameras, four Weisenberg cameras, a rotating anode x-ray generator, a powder diffractometer with automated data output, and a fully automated 4-circle diffractometer.) The capabilities also exist to pursue most crystallographic studies at elevated temperatures, to about 900 C.

One investigation which has been underway here for some time concerns the crystallographic details of the Jahn-Teller distortion in housmannite (Mn_3O_4). Although only some of the earliest work on this problem has been published (Ishii et al., 1972; Yamanaka and Nakahira, 1973), considerable progress has been made in recent years. At elevated temperatures (>900 C) the tetrahedral spinel structure of Mn_3O_4 undergoes a second-order phase transition to another cubic structure. Extensive measurements on materials spanning the entire solid solution compositional range of $Mn_xFe_{3-x}O_4$ ($0 \leq x \leq 3$) have been carried out by Yamanaka and his coworkers. Combined electron density maps, Mössbauer data (with Fe^{57} as the Mössbauer source), and infrared absorption measurements have led to a realization that the so-called "cubic-form" is in fact a "bulk average" of microscopic tetragonal "domains" resulting from the Jahn-Teller distortion. It is expected that the details and very interesting conclusions of this work will be published in the near future.

As mentioned above, the high pressure studies of this group are somewhat anticipatory at present. They do have a single crystal diamond-anvil clamp cell, of the type developed by Merrill and Bassett (1974). However, their immediate plans call for development of a new diamond-anvil single crystal pressure cell--probably one with high temperature capabilities as well. Apparently budgeting for this expansion has already been allocated and implementation is imminent.

4. Geological Institute

Professor Toshimuchi Iiyama has only recently returned from more than two decades of research at the Centre de Recherches sur la Synthese et Chimie des Mineraux, C. N. R. S. in France. His work in the past has been involved with explaining various geological reactions, e.g., determination of the point

where solid solution minerals cease to be an ideal solid solution. As an example, in silicate aqueous solutions, at about 1.5 GPa, the characteristics of the melt, i.e., viscosity and density, abruptly change suggesting a phase transition in the melt (cf. Iiyama, 1974 and Iiyama and Volfinger, 1976).

Most recently at UT, a brand new hydrothermal apparatus has been installed and preliminary testing procedures were underway in early April, 1978. The apparatus consists of an Ar-gas bomb with internal heating capabilities to 600 C. Using a hydraulic ram, the Ar is compressed to about 600 MPa; increased pressurization to 1 GPa is then obtained by heating. This equipment was designed jointly by Professor Iiyama and engineers from Kobe Steel Company, Ltd., and will be used in the immediate future for studies on K and Na silicates.

5. Summary

Clearly there is an abundance of pressure related research underway at UT. By and large, the groups visited all appear to be very well funded and to have an abundance of high quality students eager to work and learn. As noted in the text, some of the most innovative and advanced programs seen in Japan are found here—especially at the Institute for Solid State Physics. Dr. Takehiko Yagi (son of Professor Kenzo Yagi of Hokkaido University — Part II-D-2) is presently completing a two-year post-doctoral program at the famed Carnegie Geophysical Laboratory in Washington, D.C. He is expected to return shortly to Professor Akimoto's laboratory at the ISSP and will undoubtedly bring much of the diamond-cell expertise back to Japan with him. (A new world record for static pressures has recently been set at the Geophysical Laboratory, Carnegie Institution of Washington: 172 GPa.)* It is reasonable to expect a significant growth in this area at the UT, a growth which will, more than likely, expand into high pressure laboratories located throughout Japan and the world.

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III. HIGHLIGHTS

A. INTRODUCTION

In this final section, an effort is made to highlight some of the high pressure programs encountered during this three month sojourn which, in the opinion of this reviewer, are worthy of special note. The descriptions here are intentionally very brief but additional information can be found in the main text (Part II); the reader is referred to the Japanese scientists themselves for complete details (institutional addresses are given in Appendix D).

The high pressure research programs are subdivided into two categories: those directed primarily toward the development of new or improved apparatus, which include, inter alia, ultra-hard materials synthesis, and those with specific scientific research objectives.

B. APPARATUS DEVELOPMENT

1. Equipment

In the category of large working volume high pressure apparatus development, perhaps the system in Japan capable of producing the largest compressive force and devoted exclusively to high pressure research is the 15,000-ton press of Professor Kawai at Osaka University. In addition to fundamental research problems, this facility is being used for both development of improved designs of the final anvil assembly and for synthesis of sintered diamond compacts. An equally impressive program, supported by a brand new 10,000-ton press at Nagoya University, is that of Professor Kumazawa to continue the development of his multiple-anvil-sliding-system (MASS) in which perhaps static, large volume pressures exceeding (100 GPa) may be realized. In discussing large volume hydraulic systems, Professor Akimoto's laboratory at The University of Tokyo (Institute for Solid State Physics) should be noted; examples of most every piece of modern high pressure apparatus are in use and a new split-cylinder multi-stage system is under development. In the adjacent office at The University of Tokyo, Professor Minomura heads a team responsible for the design and construction of what appears to be the first Japanese diamond-anvil cell, the so-called "Ken-ichi cell." This cell has been routinely operated to pressures in excess of 20 GPa.

One piece of equipment being used in conjunction with high pressure x-ray studies is the position sensitive proportional counter. Developed by Professor Yamada at Osaka University, he and Professor Minomura have employed this detector recently to monitor the high pressure structure of iodine. The system is also currently in use at Kyushu University by Professor Takemura's group for high pressure investigation of polyvinylidene fluoride.

Variable temperature facilities are a common sight in most Japanese high pressure laboratories, but usually for operation above ambient temperatures; only two very low temperature devices were seen in Japan. One was developed under the guidance of Professor Fujii at The University of Tokyo: here a Bridgman anvil clamp cell has been coupled to a dilution

refrigerator and pressures approaching 10 GPa can be maintained at temperatures down to 30 mK. The other system is in operation in the Physics Department of Hokkaido University where simultaneous electrical resistivity and x-ray scattering experiments can be performed to 15 GPa and 4.2 K.

2. SUPER-HARD MATERIALS SYNTHESIS

In the area of super-hard materials synthesis, two items are deserving of note: first are the achievements of Professor Sawaoka and his co-workers at the Tokyo Institute of Technology. This team has succeed in fabricating a sintered cubic boron nitride compact without the need of a binding material. Tests of this material for high pressure anvil applications are already underway. Another program that may produce a significant advancement in the state-of-the-art of super-hard materials synthesis is that being pursued by Dr. Inoue and his co-workers at Kobe Steel, Ltd. For perhaps the first time, in situ, x-ray studies are being used to monitor the reactants during the synthesis process. Work is underway on both boron nitride and diamond compacts and the preliminary data have raised some very curious questions, e.g.: Why has diamond been observed to convert to graphite in a region of the phase diagram where the diamond phase is presumed to be stable?

C. SCIENTIFIC RESEARCH

One of the more novel ideas in high pressure research today is the application of extended x-ray absorption fine structure (EXAFS) measurements. As has been recently shown, careful x-ray measurements near an absorption edge can yield detailed information about chemical bonds, interatomic spacings, and atomic vibrations.* Currently the Kenichi diamond-anvil cell is being used by scientists from The University of Tokyo at the Stanford Synchrotron Radiation Laboratory to carryout EXAFS measurements on Ni.

Another very current research investigation of note is the multiple, pressure induced phase transition in MnNiGe by Professor Ansai of Keio University and Dr. Ozawa of the Japan Atomic Energy Research Institute. Work is underway to investigate the interconnection between the first-order structural transition and the second-order magnetic transition in this system. The triple point is estimated to be at 0.3-0.4 GPa and 350 K.

An interesting program underway in the geophysical area is that of Professor Hariya and co-workers at Hokkaido University. They are measuring the pressure dependence of the deuterium-to-hydrogen ratio in selected silicates and attempting to correlate this information with the role of water in the mantle and lower crust.

The apparent existence of a hysteresis loop in certain alkali halides is an observation currently being examined in detail by Professor Fujiwara and his group at Hiroshima University. In a hydrostatic pressure environment, they have observed that the transition pressure in KCl, under equilibrium conditions, ranges from 2.53 to 1.66 GPa on cycling.

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*Ref.: Ingalls, R., Garcia, G. A., and Stern, E. A. (1978) Phys. Rev. Lett. 40, 334.

D. PHILOSOPHICAL COMMENT

The high pressure research community in Japan seen by this reviewer appeared to be in a healthy state. It was very difficult to get precise information regarding funding, but most of the groups visited gave all appearances of being reasonably well off. As is probably the case anywhere in the world, the groups using the newest equipment and supporting the broadest research programs, tended to be located at the more renown and prestigious institutions.

A criticism offered in a most constructive spirit, concerns the possible stifling of creativity among the younger Japanese scientists. It seemed as if, in many cases, programs were directed from the top down, based on relatively little council with the "bench scientist." In other words, the senior program director was often a scientist who, because of several years operating at the managerial level, might be out of the "main stream of research" in his field and yet, it was he who decided policy. And, because of the great respect accorded by the Japanese to their senior personnel, it is very difficult for a junior research scientist to voice objections or criticize the actions of those above him.

In this same context, I found the Japanese research community, perhaps like Japan itself, to be a rather conservative, ultra-stable environment. In this society a man was hired essentially, for life, i.e., barring exceptional circumstance, a scientist does not "job hop" in Japan. This has both positive and negative effects. On one hand, it provides a very stable environment in which a scientist can devote his mental energies exclusively to the problems of research without anguishing over his personal "job security," but, on the other hand, it tends to eliminate some of the motivation that stems from personal competition and the desire for advancement. This is not to say that the high pressure research community in Japan is devoid of competition-- indeed I sensed very strong feelings of pride and a "friendly competitive spirit" between the "east" and the "west" - the former being represented by The University of Tokyo and the latter by Kyoto and Osaka Universities. Moreover, to the betterment of all, there appears to be ample opportunity for dialogue and information exchange within the Japanese high pressure community (cf. Appendix B).

It also seemed to this reviewer that there were very few laboratory technicians available to the Japanese high pressure scientist, i.e., at many research laboratories, if graduate student services were not available, it was incumbent upon the staff scientists to perform vitrually all facets of a research program personally, in some cases, even down to typing the final manuscript for publication.

Generally speaking, scientists at one laboratory were conversantly familar with the details of the work of their fellow scientists at other institutions and it was not entirely uncommon to see programs of collaboration underway between different groups.

It also appeared that many Japanese scientists, at an early point in their career, spend one to two years working in either the United States or European laboratories to broaden their background. Following these sabbatical or post-doctoral studies, they return to Japan to practice their profession.

All in all, the Japanese high pressure community is definitely on the forefront in many areas of high pressure research today. This is not only evidenced by the research currently underway and the development of the MASS and split-sphere apparatus, but by Japan's role in supporting international high pressure conferences, to wit: The Fourth International High Pressure Conference (Kyoto, Japan; 25-29 November 1974); United States -Japan joint seminar, High Pressure Research: Application in Geophysics (Honolulu, Hawaii; 6-9 July 1976); International Geodynamics Conference (Tokyo, Japan; 13-17 March, 1978). Moreover, at the most recent AIRAPT conference*, of the twenty-two participating countries, Japan was the second-most prolific in terms of contributed papers surpassed only by the hosting country, the United States.

The state of high pressure science and technology in Japan today is very healthy. Prospects for continued growth and advancement are good - this is especially true in the area of large volume apparatus. It is very possible that the first static megabar pressures in volumes as large as several cm^3 may be realized in Japan within the next few years.

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*Sixth International Conference on High Pressure, Boulder, Colorado; 25-29 July, 1977

Appendix A: SUPER-HARD MATERIALS SYNTHESIS PROJECT

There is a rather limited program, sponsored by the Japanese government, to synthesize super-hard materials. The objective of this program is not to produce a single final product, but rather to carryout basic materials research with particular emphasis on appropriate sintering mechanisms. Efforts are directed toward super-hard and high thermal conductivity materials; at present special emphasis is given to both synthetic diamond and cubic-BN. Some of the scientists receiving partial support under this program include Dr. Funaga of The National Institute for Researches on Inorganic Materials, Professor Osugi of Kyoto University, Professor Koisumi of Osaka Univeristy, Dr. Inoue of Kobe Steel, Ltd. and Dr. Nakayama of the Nagoya Institute for Industrial Research; people at Sumitomo Electric Industries are acting as agents.

Curiously, some of the most recent progress in this area, viz a sintered very hard BN-compact without a binder, has been made by Professor Sawaoka and his staff at Tokyo Institute of Technology who are working in collaboration with the Nippon Oil and Fats Company, Ltd, although the budget at Tokyo Institute of Technology for this work is very limited.

Appendix B: HIGH PRESSURE ORGANIZATIONS

There are at present four organizations in Japan expressly concerned with the development and furtherance of high pressure research and technology. The Japanese High Pressure Institute is interested, inter alia, in large scale utilization of high pressure technology; applications such as boilers, reactor containers, and large scale extrusion presses are of primary interest to this group headed by Professor Hirosh Kihara of Osaka University. Every two months the Japanese High Pressure Institute publishes a journal entitled "Pressure Engineering."

The Japan Society for the Promotion of Science is supported by the Ministry of Education and consists of a large number of divisions; Division No. 138 is known as the High Pressure Division. This group is in its ninth year and is currently headed by Professor E. Udoguchi of Chiba University. The organization has, as one of its primary functions, the provision of travel funds for scientific purposes, i.e., to both invite foreign scientists to Japan and to send their Japanese counterparts abroad. All divisions within the Japan Society for the Promotion of Science are reviewed every five years; next year the High Pressure Division will be reviewed and hopefully refunded for another half-decade.

A third group is the Japan Society for Materials Science; largely active in the Kyoto area, this group is currently headed by Dr. Yoshimasa Takezake of the Institute of Chemical Research at Kyoto University, a new group leader is selected every two years. This group hosts meetings periodically and invites speakers to present seminars on all aspects of high pressure work. Usually the speakers distribute abstracts of their presentations.

The fourth organization, and perhaps the most useful in terms of disseminating information, is the Japanese High Pressure Conference. This meeting is held annually in Japan at a site which moves from laboratory to laboratory. The first meeting was held at Kyoto University and the 1978 conference is scheduled to be held at Tohoku University at Sendai this October. This will be the 19th meeting of the group and, as is the custom, the proceedings, usually a one or two page summary of each paper, will be published, but only in Japanese. (Up until a few years ago, Dr. Leo Merrill of the High Pressure Data Center at Brigham Young University was publishing this information in English.) The intent is to keep these meetings very informal and frequently to report "work in progress." Formal reports of completed work are subsequently submitted to the refereed literature for publication in due time. Approximately one-third of the papers presented at the most recent meeting have already been published in the open literature.

Appendix C: HIGH PRESSURE SCIENTISTS*

ABE, Shinya(W)

AKAISHI, Minoru(O)

AKAOGI, Masaki(Z)

AKIMOTO, Shunichi(Z)

ANZAI, Shuichiro(F)

ARIMA, Makoto(D)

ASADA, Tsunesaburo(G)

ASAI, Kenjiro(J)

ASAUMI, Katsuyuki(Z)

ATSUKAWA, Morishige(T)

ENDO, Hirohisa(J)

ENDO, Shoichi(S)

ENDO, Tadashi(O)

ENOSHITA, Ryosuke(K)

FUJII, Genshiro(Z)

FUJII, Hironobu(B)

FUJII, T.(J)

FUJII, Toshitsugu(Z)

FUJII, Yasuhiko(Z)

FUJISHIRO, Ikuya(M)

FUJIMOTO, Sanji(A)

FUJISHITA, Kaori(H)

FUJITA, Taketoshi(O)

FUJIWARA, Hiroshi(B)

FUKUNAGA, Osamu(O)

FUKUYAMA, Hiroyuki(Z)

GESI, Kazuo(E)

GOTO, Tsuneaki(W)

HAGA, Nobuhiko(Z)

HAGIO, Tsuyoshi(N)

HAMANOUE, Kumao(I)

HAMAYA, Nozomu(Z)

HARA, Kimihiko(J)

HARA, Yoji(Z)

HARIYA, Yu(D)

HASEGAWA, Akio(M)

HASHIMOTO, N.(X)

HINATA, Masanori(V)

HORI, Shinichi(I)

HORIGUCHI, M.(J)

HOSOYA, Sukeaki(Z)

IBONAI, Masaru(T)

IDO, Masayuki(D)

IIO, S.(X)

IIYAMA, Toshimichi(Z)

IKEDA, Tsutomu(G)

IMADA, Kiyohisa(K)

IMAOKA, K.(X)

INOUE, Katsuhiko(G)

ISHIBASHI, Yoshihiro(M)

ISHIDA, Katsuhiko(J)

ISHIHARA, I.(J)

ISHII, M.(Z)

ITO, Keisuke(H)

ITO, Eiji(Q)

ITO, Taisuke(I)

IWASAKI, Hiroshi(W)

IWATA, Minoru(O)

KADOMATSU, Hideoki(B)

KAJIYAMA, Tisato(K)

KAMIGAKI, Kazuo(W)

KANADA, Hisao(O)

KANEKO, Takejiro(W)

KANETSUNA, Nisaaki(T)

KASHIWAGI, Hiroshi(H)

KATANO, Susumu(D)

KATAOKA, T.(T)

KATAYAMA, Masatuke(J)

KATO, M.(M)

KATO, Masao(T)

KAWADA, Kaoru(Z)

KAWAI, Naoto(S)

KAWAKITA, Takao(V)

KAWAMURA, Katsuyuki(Z)

KAWASAKI, Toshisuke(J)

KIJIMA, Junichi(F)

KINOMURA, N.(S)

KITANO, T.(T)

KOBAYASHI, Kazuo(N)

KODAIRA, Kohei(D)

KOGA, Kazunori(K)

KOJIMA, Masaki(R)

KOJIMA, Seiji(Z)

KOIZUMI, Mitsue(S)

KONDO, Kenichi(X)

KUBOTA, Hironobu(H)

KUME, S.(S)

KUSHIRO, Ikuo(Z)

KUZUBA, Takashi(O)

KYOTANI, Mutsumasa(T)

MAEDA, Itaru(D)

MAEDA, Yoji(T)

MAEKAWA, Y.(J)

MAKITA, Tadashi(H)

MANKI, Yoshiaki(I)

MARUYAMA, Seiichiro(K)

MASHIMO, T.(X)

MATSUBARA, Y.(J)

MATSUI, Yoshito(Q)

MATSUMOTO, Kiyoichi(I)

MATSUO, Shigenobu(H)

MATSUSHIGE, Kazumi(K)

MATSUSHIMA, Shogo(J)

MATSUSHITA, Toru(D)

MIDORIKAWA, Michio(M)

MINOMURA, Shigeru(Z)

MISONOU, Masao(J)

MIYAJI, Hideki(J)

MIYAMOTO, Y.(S)

MIYAMOTO, Yasuhiko(K)

MIYAZAKI, Kenji(N)

MIZUNO, Tooru(A)

MŌRI, Nobuo(D)

MŪSHIAGE, Masato(J)

NAGANO, Hiroshi(Z)

NAGASHIMA, Akira(F)

NAKA, Shigeharu(M)

NAGATA, Kiyofumi(K)

NAKAFUKU, Chitoshi(K)

NAKAGAWA, Yasuaki(W)

NAKAGIRI, Nobuyuki(B)

NAKAHARA, Masaru(J)

NAKAHIRA, M.(Z)

NAKAJIMA, Tadashi(S)

NAKAJIMA, Takayoshi(M)

NAKAMURA, K.(K)

NAKAMURA, Terutaro(Z)

NAKANO, T.(J)

NAKATANI, H.(J)

NAKAUE, Akimitsu(G)

NAKAYAMA, Kazuo(T)

NAKAZAWA, Hiromoto(O)

NISHIBATA, Ken(P)

NISHIMOTO, N.(X)

NOGUCHI, Kenji(T)

NOMURA, Motoyuki(B)

OBA, Takanobu(D)

ODA, Yasukage(Z)

OGAWA, Ichitaro(N)

OGO, Yoshiaki(R)

OGURI, Akio(A)

OHASHI, Haruo(O)

OHASHI, Masayoshi(W)

OHNISHI, S.(T)

OHTA, Satoru(F)

OHTANI, Eiji(M)

OKA, Yasutami(D)

OKADA, Akira(T)

OKAI, Bin(O)

OKAMOTO, M.(J)

OKAMOTO, Motohide(A)

OKAMOTO, Takeo(Z)

OKAMOTO, Tetsuhiko(B)

OKURI, Yasuhiro(R)

ONODA, Yoshito(O)

ONODERA, Akifumi(S)

OOMI, Gento(D)

OSUGI, Jiro(J)

OYANAGI, Hiroyuki(Z)

OZAWA, Kunio(E)

SAEGUSA, Shogo(F)

SAITO, Shinroku(X)

SAMBONGI, Takashi(D)

SASAKI, Muneo(J)

SATO, Haruki(F)

SATO, Masanori(I)

SAWADA, Akikatsu(M)

SAWAMOTO, Hiroshi(M)

SAWAOKA, Akira(X)

SENOO, Masafumi(M)

SETAKA, Nubuo(O)

SHIGEMATSU, Kazuyo(K)

SHIMADA, M.(S)

SHIMADA, Mitsuhiko(J)

SHIMADA, Shiro(D)

SHIMIZU, Hiroyasu(A)

SHIMIZU, K.(J)

SHIMURA, Yukio(T)

SHIRAI, Yasuharu(B)

SHIRAKI, Masaru(T)

SHIROTANI, Ichimin(Z)

SŌMIYA, Shigeyuki(X)

SUGITA, Nobuyuki(J)

SUGIURA, H.(X)

SUITO, Kaichi(S)

SUMI, Kazunori(A)

SUMINO, Yoshio(M)

SUSA, Kenzo(C)

SUZUKI, Keizo(U)

SUZUKI, Norio(G)

SYONO, Yasuhiko(W)

TAKAGI, Toshiharu(I)

TAKAGI, Yutaka(M)

TAKAHASHI, Eiichi(Z)

TAKAHASHI, T.(J)

TAKAMIZAWA, Kanichiro(K)

TAKAYAMA, H.(T)

TAKAYANAGI, Motowo(K)

TAKEDA, Yasuo(M)

TAKEMURA, Kenichi(Z)

TAKEMURA, Tetuo(K)

TAKEUCHI, Yoshio(Z)

TAKEZAKI, Yoshimasa(J)

TAKI, Seiji(K)

TAKUBO, H.(S)

TAMURA, Kozaburo(J)

TAMURA, Syuzo(O)

TANABE, Tomoko(T)

TANAKA, F.(J)

TANAKA, Yoshio(T)

TANAKA, Yoshiyuki(H)

TANIGUCHI, Yoshihiro(U)

TERADO, TOSHIHIKO(A)

TERANISHI, Hiroshi(I)

TOGAYA, Motohiro(S)

TOMIZUKA, Isao(T)

TSUBOI, Shigemi(A)

TSUCHIYA, Masao(L)

TSUCHIYAMA, Akira(Z)

TSUDA, Nubuo(O)

TSUJI, Kazuhiko(J)

TSUJI, Kazuhiko(Z)

TSUNASHIMA, Itaru(D)

TSUZUKI, T.(J)

UEMATSU, Masahiko(F)

UKAI, Hitoshi(A)

UNEO, M.(J)

UOSAKI, Y.(J)

UTSUMI, Nobuo(I)

WAKATUSUKI, Masao(Y)

WATANABE, Hiroshi(J)

WATANABE, Koichi(F)

WATANABE, Mamoru(O)

WATANABE, Tadahiko(N)

WATANABE, Takashi(D)

YAGI, Takehiko(Z)

YAGI, Yoshiro(G)

YAMADA, Hiroshi(A)

YAMADA, Takeshi(I)

YAMAMOTO, Kazuo(Z)

YAMAMOTO, Shigeru(M)

YAMAMOTO, Shojiro(P)

YAMAMOTO, Takashi(J)

YAMAMOTO, Yoshiaki(B)

YAMANAKA, Takamitsu(Z)

YAMAOKA, *Shinobu(O)*

YAMAUCHI, K. (V)

YAO, Makoto(J)

YASUDA, NAOHIKO(A)

YASUMIWA, Munehisa(K)

YATA, Junzo(I)

YOSHIDA, Hajime(W)

YOSHIMOTO, Jiichiro(O)

YOSHIZUMI, Tsuneto(K)

YUKUTAKE, Hideo(J)

*The letter in parentheses following each name corresponds to the institution identified in Appendix D.

Appendix D: VISITATION LIST

Institution	Laboratory	Host(s)
A. GIFU UNIVERSITY Nakamonzen-cho Kagamigahara-shi Gifu 504, JAPAN	Dept.of Electrical Engineering	Prof. Sanji Fujimoto
B. HIROSHIMA UNIV. 1-1-89, Higashisenda-machi Hiroshima 730, JAPAN	Dept. of Materials Science	Prof. Hiroshi Fujiwara
C. HITACHI LTD. P.O. Box 2 Kokuhbunjl, Tokyo JAPAN 185	Central Research Laboratory	Dr. Kenzo Susa
D. HOKKAIDO UNIV. Nishi-8-Chome, Kita-10-Jo, Kita-ku Sapporo 060, JAPAN	Dept. of Geology & Mineralogy Dept. of Physics	Prof. Kenzo Yagi & Prof. Y. Hariya Mr. T. Watanabe
E. JAPAN ATOMIC ENERGY RESEARCH INSTITUTE Tokai, Ibaraki 319-11, JAPAN	Solid State Physics Laboratory	Dr. Kunio Ozawa
F. KEIO UNIVERSITY 3-14-1 Hiyoshi Kohoku-ku Yokohama 223, JAPAN	Dept. of Mechanical Engineering Dept. of Applied Chemistry	Prof. Masahiko Uematsu Prof. Shuichiro Anzai
G. KOBE STEEL, LTD. 53-3, Aza-Maruyama Gomo, Nada-ku Kobe 657, JAPAN	Asada Research Laboratory	Dr. Katsuhiko Inoue
H. KOBE UNIVERSITY Rokkodai, Nada-ku Kobe 657, JAPAN	Dept. of Chemical Engineering Dept. of Earth Sciences	Prof. Tadashi Makita Prof. Keisuke Ito
I. KYOTO INSTITUTE OF TECHNOLOGY Matsugasaki, Sakyo-ku Kyoto 606, JAPAN	Dept. of Chemistry Dept. of Analytical Chemistry	Prof. Taisuke Ito Prof. Masanori Sato
J. KYOTO UNIVERSITY Oiwake-cho, Kitashirakawa, Sakyo-ku, Kyoto 606, JAPAN	Dept. of Chemistry Dept. of Physics Geophysical Institute Abuyama Seismological Observtry.	Prof. Jiro Osugi Prof. Kenjiro Asai & Prof. Hirohisa Endo Prof. Hideo Yukutake Prof. Mitsuhiko Shimada

Institution	Laboratory	Host(s)
K. KYUSHU UNIVERSITY 3576 Hakozaki, Higashi-ku Fukuoka 812, JAPAN	Dept. of Applied Science Dept. of Applied Chemistry Dept. of Electrical Engineering	Prof. Tetuo Takemura Prof. Motowo Takayanagi Prof. Irie
L. NAGASAKI INSTITUTE OF TECHNOLOGY 536 Aba-machi Nagasaki 851-01, JAPAN	Dept. of Chemistry	Prof. Masai Tsuchiya
M. NAGOYA UNIVERSITY Furo-cho, Chikusa-ku Nagoya 464, JAPAN	Dept.of Earth Sciences Dept. of Mechanical Engineering Synthetic Crystal Research Lab.	Prof. Mineo Kumazawa Prof. Ikuya Fujishiro Prof. Yoshihiro Ishibashi & Prof. Akikatsu Sawada
N. NATIONAL INDUSTRIAL RESEARCH INSTITUTE OF KYUSHU Shuku-machi, Tosu-shi Saga-Ken 814, JAPAN	Metals & Machine Division	Dr. Kazuo Kobayashi
O. NATIONAL INSTITUTE FOR RESEARCHES IN INORGANIC MATERIALS Sakura-mura, Niihari-gun Ibaraki 300-31, JAPAN	5th, 6th, & 8th Research Grps.	Dr. Bin Okai
P. NATIONAL RESEARCH LABORATORY OF METROLOGY 10-4, 1-chome, Kaga Itabashi-ku, Tokyo 173 JAPAN	Mechanical Metrology Section Thermal Measurement Section	Mr. Ken Nishibata Dr. Kiyoto Mitsui
Q. OKAYAMA UNIVERSITY 827, Yamada, Misasa-cho Tohaku-gun, Tottori-ken 682-02, JAPAN	Institute for Thermal Spring Research	Dr. Yoshito Matsui & Dr. Eiji Ito
R. OSAKA CITY UNIV. 459, Sugimoto-cho, Sumiyoshi-ku Osaka 558, JAPAN	Dept. of Applied Chemistry	Prof. Yoshiaki Ogo
S. OSAKA UNIVERSITY V-1, Machikaneyama-cho Toyonaka, Osaka 560 JAPAN	Dept. of Materials Physics Inst. of Scientific and Industrial Research College of General Educations	Prof. Naoto Kawai & Prof. Akifumi Onodera Prof. M. Koizumi Prof. Y. Yamada & Prof. S. Kume

Institution	Laboratory	Host(s)
T. RESEARCH INSTITUTE FOR POLYMERS AND TEXTILES 4 Sawatari, Kanagawa Yokohama 221, JAPAN	Chemistry of Polymers & Text. Physics & Engineering of Polymers and Textiles	Dr. Yoshio Tanaka Dr. Hisaaki Kanetsuna
U. RITSUMEIKAN UNIV. Tojiin-Kitahachi, Kita-ku Kyoto, 603 JAPAN	Dept. of Chemistry	Prof. Keizo Suzuki
V. SUMITOMO ELECTRIC INDUSTRIES, LTD. 1-3, Shimaya, 1-chome Konohana-ku, Osaka 554, JAPAN	Metallurgical Research Sect.	Dr. Masanori Hinata Dr. Takao Kawakita
W. TOHOKU UNIVERSITY 1-1-2, Katahira, Sendai 980, JAPAN	Research Institute for Iron, Steel and Other Metals	Prof. Hiroshi Iwasaki Prof. T. Goto Prof. Kazuo Kamigaki
X. TOKYO INSTITUTE OF TECHNOLOGY Ookayama, Meguro-ku Tokyo 152, JAPAN	Research Laboratory of Engineering Materials	Prof. Akara Sawaoka Prof. S. Somiya
Y. TOKYO SHIBAURA ELECTRIC CO. Toshiba-cho, komukae, Saiwai-ku, Kawasaki 210, JAPAN	Toshiba R & D Center	Dr. Masao Wakatsuki
Z. UNIVERSITY OF TOKYO 1-22-7, Roppongi, Minato-ku Tokyo 106, JAPAN	Institute for Solid State Phys. Mineralogical Institute Geological Institute	Prof. Shigeru Minomura Prof. S. Akimoto Prof. Fujii Prof. Y. Takeuchi Prof. Iiyama

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